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Bulletin 693

# THE EVAPORATION AND CONCENTRATION OF WATERS ASSOCIATED WITH PETROLEUM AND NATURAL GAS

BY

R. VAN A. MILLS

AND

ROGER C. WELLS

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# THE EVAPORATION AND CONCENTRATION OF WATERS ASSOCIATED WITH PETROLEUM AND NATURAL GAS.

By R. Van A. Mills and R. C. Wells.

## INTRODUCTION.

### RESULTS OF THE INVESTIGATION.

The association of saline waters[1] with petroleum and natural gas has been widely observed, but the origin or mode of formation of these waters has remained a perplexing problem. It has been commonly assumed that the dissolved salts were derived through the leaching of the sediments by percolating ground waters, or that the deep-seated brines are essentially fossil ocean waters which were included and buried in the marine sediments at the time of deposition. In the light of the present investigation these relatively simple concepts give way to the conclusion that the brines are the result of a complex and long-continued evolution in which waters of sedimentation together with ground waters from other sources have undergone deep-seated evaporation and concentration accompanied by noteworthy chemical changes.

Our interpretation of the mode of formation of many oil and gas field brines is partly the outcome of a study of changes in the brines incident to the extraction of gas and oil from their reservoir rocks. It appears that the waters undergo deep-seated concentration, brought about by their evaporation into moving and expanding gas. During this concentration there is a definite order of change in the relative proportions of the dissolved constituents in the waters. Carbon dioxide and other gases are lost from solution. Calcium, magnesium, and iron separate from solution as carbonates, and under favorable conditions sodium and minor proportions of calcium and magnesium separate as chlorides—a process illustrated in the salting up of gas wells. A further separation of the dissolved constituents, more particularly of calcium, magnesium, iron, sodium, barium, strontium, carbonate, and silica, is brought about when waters from different beds and having different properties of reaction become mixed. Lastly, the ratio of calcium to chlorine in the waters increases and the ratio of sodium to chlorine decreases with the concentration.

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[1] The term water is frequently used throughout this paper to mean a dilute aqueous solution or weak brine.

It is a logical step to pass from the facts just recorded to a theory of the formation of the brines. The brines, as they occur in their reservoir rocks, prior to the extraction of gas and oil from these rocks by man, vary greatly in their degree of concentration, and it may be stated as a rule that the concentration of the dissolved constituents of the waters increases with depth, and that the differences between the concentrated and relatively dilute waters are of the same sort as those brought about during the artificial extraction of gas and oil. There are, however, noteworthy exceptions to this rule; waters that appear to have remained deeply buried under thick covers of relatively impermeable beds since their inclusion in the sediments seem to be less concentrated than those occurring in more shallow beds directly beneath and above certain unconformities.

We are led to conclude that the changes in the waters incident to the extraction of gas and oil are largely of the same order as those by which the brines were formed. Marine water of sedimentation and ground water from other sources have been included and deeply buried in the sediments, where, in association with gas and oil, they have migrated and undergone concentration, accompanied by changes in the nature and relative proportions of the dissolved constituents. Concentration is due in part to the leaching of the sediments by the migrating waters but mainly to the evaporation of water into gases that are moving and expanding through natural channels. Reactions between the dissolved constituents of different types of waters and between the dissolved constituents of the waters and the organic and inorganic constituents of the sediments have been important factors in the formation of the brines and so also have mass action and reactions due to deep-seated thermal conditions.

During the deep-seated concentration of the waters various constituents have separated from solution as their points of saturation were reached. Under favorable conditions the concentration has proceeded sufficiently to cause the deposition from solution of sodium chloride. Chemical reactions and precipitation have also been effective in bringing about these separations. Much evidence of what has taken place through deep-seated natural agencies is furnished by studies of the salts interstitially included in the sediments from which gas and oil have not been extracted, but the most striking example of the deep-seated natural deposition of salt is furnished by the salt domes of Louisiana and Texas. We attribute the formation of these great salt masses largely to the geophysical and geochemical processes herein described; deep-seated evaporation and concentration of chloride waters due to the movement and expansion of gases through natural passages, more particularly through fault fissures, having been agencies of prime importance.

The salts deposited in wells during the extraction of gas and oil, those occurring interstitially in the sediments, and those constituting the Louisiana and Texas salt domes all agree closely in composition with hypothetical salts whose loss from solution during concentration has been predicated by us through comparisons of the analyses of the dilute and concentrated brines under scrutiny.

It is our purpose to describe the mode of concentration of these waters, the changes they have undergone, and some of the relations that the changes bear to the occurrence and production of petroleum and natural gas. Though samples of the waters under investigation were collected only in the Appalachian fields, the conclusions are widely applicable.

As shown in the concluding chapter, many of the principles herein set forth are capable of practical application, and it is intended that this bulletin shall be of economic value to oil and gas operators as well as of scientific interest. We shall feel repaid for our studies if we make apparent the need for further detailed field and laboratory investigations of the chemical and physical interactions between petroleum and natural gas, on the one hand, and the associated waters and reservoir rocks, on the other.

## ACKNOWLEDGMENTS.

We are indebted to our colleagues D. Dale Condit and G. B. Richardson for cooperation and assistance during the field investigations relative to this paper, and to M. I. Goldman for petrographic studies of rock specimens. E. S. Larsen and W. T. Schaller have also made brief petrographic examinations of some of the rock and mineral specimens collected. A. F. Melcher made the porosity tests and S. C. Dinsmore many of the water analyses herein published. The hearty cooperation of numerous oil and gas companies and individual operators is also gratefully acknowledged. To Herman Stabler and Chase Palmer we are especially indebted for assistance during the chemical investigation of materials collected in the field and for helpful criticism and advice during the preparation of the manuscript.

## FIELD WORK.

The field investigations upon which this paper is based were made by R. Van A. Mills, D. Dale Condit, Frank Reeves, and G. B. Richardson during the summers of 1914, 1915, and 1916. The oil and gas resources of the Woodsfield and Summerfield quadrangles, in southeastern Ohio, were studied by Messrs. Condit, Mills, and Reeves for four months during the summer of 1914. Subsequently the field work in these areas was continued by Mr. Mills during April and May, 1915, and June, 1916. Messrs. Richardson and Mills also studied the oil and gas resources of the Butler and Zelienople quadrangles, in western Pennsylvania, during the summer of 1915.

In the course of these economic investigations particular attention was paid to the distribution and mode of occurrence of the water associated with petroleum and natural gas, with a view to studying some of the physical and chemical relations between the hydrocarbons, the reservoir rocks, and the associated waters. As material for use in studying the possible changes that the waters have undergone, both before and after the extraction of oil and gas commenced, samples of oil, gas, oil and gas bearing rocks, and the waters associated with the oil and gas were collected for laboratory study.

The oil samples were collected fresh as the oil emerged from the wells and were placed in glass bottles for shipment. The gas samples were collected in large glass containers by the displacement of air and also by the displacement of water.

In collecting water samples from deep wells it is difficult to obtain a truly representative sample from a particular bed. Water from one sandstone is likely to enter another through poorly plugged, abandoned wells, or through and around faulty casings. The effort was therefore made to collect samples from tightly cased wells and in newly drilled fields, where water from shallow sources had not leaked into the deeper sands through abandoned wells. The samples were collected directly as the waters came from the wells and were therefore not affected by standing in tanks. So far as possible, the samples of water were collected where collateral data regarding the depth, thickness, texture, and structure of the productive sands, the geology of the region, and the history of production were available.

The rock samples were collected when they were freshly removed from the wells, except where otherwise noted. Lump samples and loose sand blasted from the deep beds when the wells were shot were collected in preference to the finely pulverized fragments contained in drill sludge.

### LOCATION OF QUADRANGLES STUDIED.

The location of the four quadrangles studied is shown on the index map (fig. 1). The Woodsfield and Summerfield quadrangles, which include parts of Belmont, Monroe, Noble, and Guernsey counties, in southeastern Ohio, are from 25 to 45 miles southwest of Wheeling, W. Va., and from 25 to 40 miles north of Marietta, Ohio. The Butler and Zelienople quadrangles, including parts of Butler, Lawrence, and Beaver counties, in western Pennsylvania, are from 20 to 40 miles north of Pittsburgh, Pa., and about 80 miles northeast of the Woodsfield and Summerfield quadrangles.

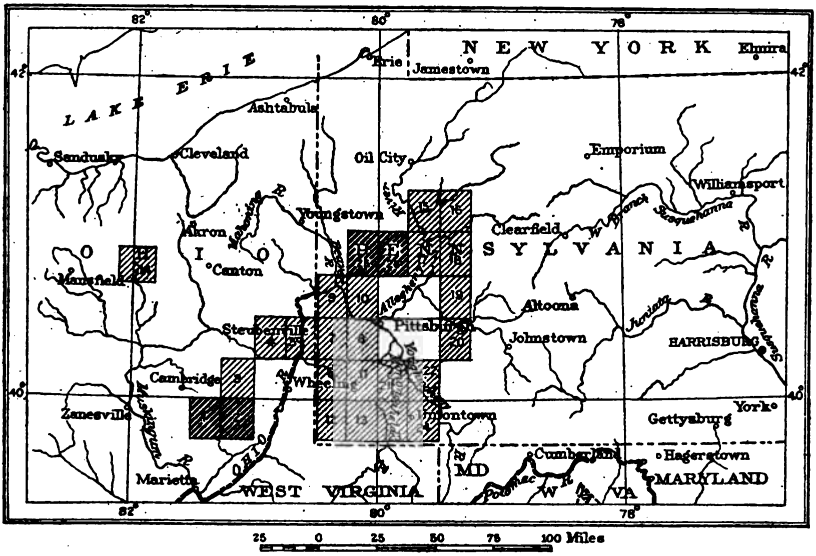

FIGURE 1.—Index map showing location of the Summerfield and Woodsfield quadrangles, Ohio (Nos. 1 and 2, heavily shaded), the Zelienople and Butler quadrangles, Pa. (Nos. 25 and 26, heavily shaded), and the names and positions of other quadrangles for which structural maps have been prepared (light shading). 3, Flushing; 4, Cadiz; 5, Steubenville; 6, Claysville; 7, Burgettstown; 8, Carnegie; 9, Beaver; 10, Sewickley; 11, Amity; 12, Rogersville; 13, Waynesburg; 14, Wooster; 15, Foxburg; 16, Clarion; 17, Kittanning; 18, Rural Valley; 19, Elders Ridge; 20, Latrobe; 21, Brownsville, 22, Connellsville; 23, Masontown; 24, Uniontown.

## GEOLOGY OF THE APPALACHIAN OIL AND GAS FIELDS.

### GEOLOGIC REPORTS RELATIVE TO THE AREAS STUDIED.

Two brief geologic reports on the Woodsfield and Summerfield quadrangles[1] have been published by the United States Geological

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[1] Condit, D. D., Structure of the Berea oil sand in the Summerfield quadrangle, Guernsey, Noble, and Monroe counties, Ohio: U. S. Geol. Survey Bull. 621, pp. 217–231, 1916 (Bull. 621–N); Structure of the Berea oil sand in the Woodsfield quadrangle, Belmont, Monroe, Noble, and Guernsey counties, Ohio: Idem, pp. 233–249, 1915 (Bull. 621–O).

Survey, and a more detailed report on the oil and gas resources of the same areas is now under preparation. Geologic reports on the Butler and Zelienople quadrangles are also being prepared for publication by the Survey. In addition to these, the Survey has published the following bulletins concerning oil and gas fields in Ohio, West Virginia, and Pennsylvania:

198. The Berea grit oil sand in the Cadiz quadrangle, Ohio, by W. T. Griswold. 1902. 43 pp., 1 pl.
279. Economic geology of the Kittanning and Rural Valley quadrangles, Pa., by Charles Butts. 1906. 198 pp., 11 pls.
286. Economic geology of the Beaver quadrangle, Pa. (southern Beaver and northwestern Allegheny counties), by L. H. Woolsey. 1906. 132 pp., 8 pls.
300. Economic geology of the Amity quadrangle, eastern Washington County, Pa., by F. G. Clapp. 1907. 145 pp., 8 pls.
304. Oil and gas fields of Green County, Pa., by R. W. Stone and F. G. Clapp. 1907. 110 pp., 3 pls.
318. Geology of oil and gas fields in Steubenville, Burgettstown, and Claysville quadrangles, Ohio, W. Va., and Pa., by W. T. Griswold and M. J. Munn. 1907. 196 pp., 13 pls.
346. Structure of the Berea oil sand in the Flushing quadrangle, Harrison, Belmont, and Guernsey counties, Ohio, by W. T. Griswold. 1908. 30 pp., 2 pls.
349. Economic geology of the Kenova quadrangle, Ky., Ohio., and W. Va., by W. C. Phalen. 1908. 158 pp., 6 pls.
454. Coal, oil, and gas of the Foxburg quadrangle, Pa., by E. W. Shaw and M. J. Munn. 1911. 85 pp., 10 pls.
456. Oil and gas fields of the Carnegie quadrangle, Pa., by M. J. Munn. 1911. 99 pp., 5 pls.

541–A. Oil and gas in the northern part of the Cadiz quadrangle, Ohio, by D. D. Condit. 1913. 9 pp., 1 pl.

621–H. Anticlines in the Clinton sand near Wooster, Wayne County, Ohio, by C. A. Bonine. 1915. 12 pp., 1 pl.

661–A. The Cleveland gas field, Cuyahoga County, Ohio, with a study of rock pressure, by G. S. Rogers. 1917. 68 pp., 2 pls.

The following geologic folios contain descriptions of oil and gas fields in Ohio, West Virginia, and Pennsylvania:

69. Huntington, W. Va.-Ohio, by M. R. Campbell. 1900.
72. Charleston, W. Va., by M. R. Campbell. 1901.
82. Masontown-Uniontown, Pa., by M. R. Campbell. 1902.
115. Kittanning, Pa., by Charles Butts and Frank Leverett. 1904.
121. Waynesburg, Pa., by R. W. Stone. 1905.
146. Rogersville, Pa., by F. G. Clapp. 1907.
176. Sewickley, Pa., by M. J. Munn. 1911.
177. Burgettstown-Carnegie, Pa., by E. W. Shaw and M. J. Munn. 1911.
178. Foxburg-Clarion, Pa., by E. W. Shaw, E. F. Lines, and M. J. Munn. 1911.
180. Claysville, Pa., by M. J. Munn. 1912.
184. Kenova, Ky.-W. Va.-Ohio, by W. C. Phalen. 1912.

## AREAL GEOLOGY.

The Appalachian oil and gas fields are in the great geosyncline generally known as the Appalachian coal basin, which lies between the Cincinnati anticline on the west and the Appalachian uplift on the east. Over most of the area, as shown by figure 2, the rocks exposed at the surface are of Pennsylvanian age, but Permian beds cover the center of the basin and both Mississippian and Devonian beds crop out around the edges.

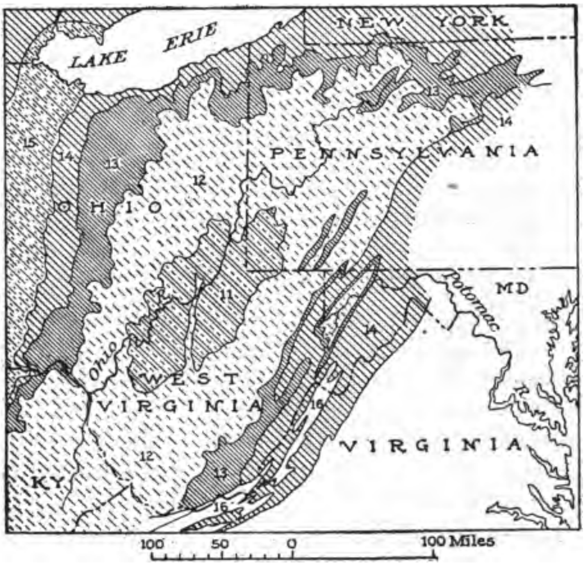


FIGURE 2.—Sketch map showing the areal geology of the Appalachian coal basin. 11, Permian; 12, Pennsylvanian; 13, Mississippian; 14, Devonian; 15, Silurian; 16, Ordovician.

## STRATIGRAPHY AND STRUCTURE.

In the fields under discussion petroleum and natural gas occur associated with saline waters in relatively porous, open-textured "pay sands" in marine deposits and in continental deposits laid down at or near sea level. The sediments in southeastern Ohio are estimated to have a total thickness of more than 9,000 feet. Some of the productive oil and gas bearing strata, such as those of the Catskill (?) formation in western Pennsylvania and those in the overlying coal measures, are probably not

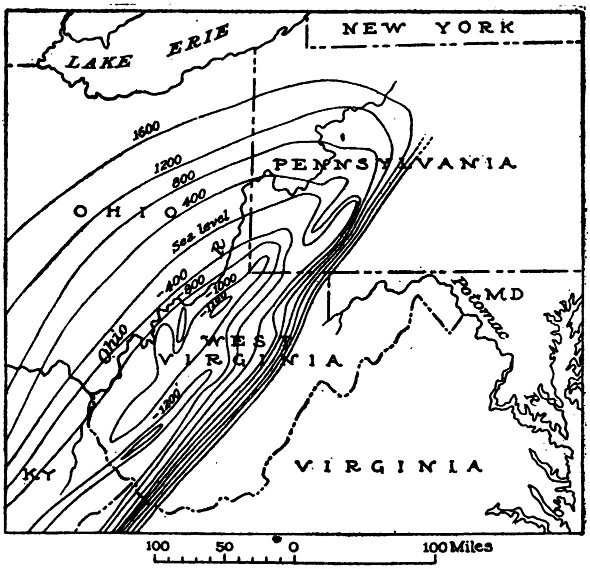


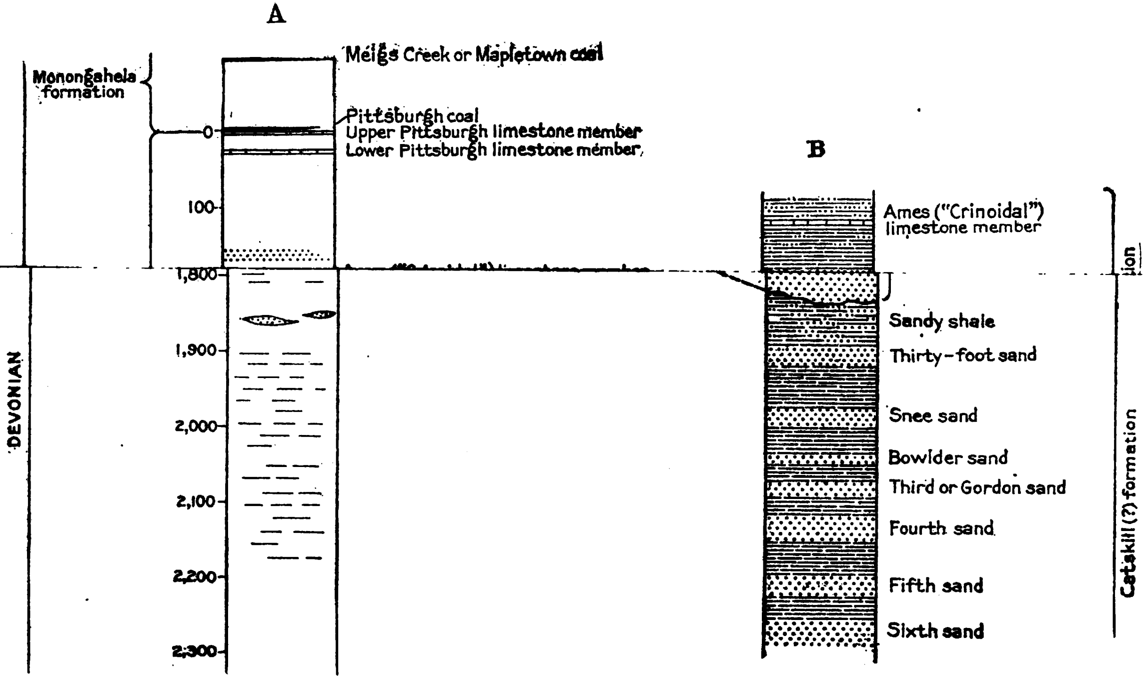
FIGURE 3.—Structure contour map of the Appalachian coal basin, showing contours on the Big Injun sand. (After Reeves.)

of marine origin, but were deposited sufficiently close to the sea to become interbedded with marine deposits. Under such conditions the nonmarine sediments have probably become more or less permeated by marine waters of sedimentation, as will be explained in the following text.

The regional structure and general position of the great Appalachian geosyncline are shown by figure 3. In the four quadrangles studied during the preparation of this bulletin (see fig. 1) the strata dip gently to the south and southeast, toward the trough of the geosyncline. The dips average approximately 50 feet to the mile, though there are numerous minor folds in which they are more pronounced. In the Woodsfield and Summerfield quadrangles, in southeastern Ohio, where a very large number of well records were procured, there is much evidence that the strata of Mississippian age had been distorted by small, relatively sharp folds prior to the deposition of the overlying Pennsylvanian sediments. Detailed studies in these two quadrangles have therefore rendered the unconformity between the beds of Mississippian and Pennsylvanian age especially evident. A generalized section of the formations in eastern Ohio is given on the following page.

The stratigraphic position of the reservoir rocks from which samples of water and of oil and gas bearing rocks were collected is shown in Plate I. It will be observed that these beds range in age from late ~~Devonian~~ to early Pennsylvanian. The oil and gas sands are for the most part lenticular, many of the productive beds at the same stratigraphic horizons being isolated from one another by relatively impermeable shales, tightly cemented sandstones, or gradations between the two.

For detailed descriptions and structure contour maps of the oil and gas sands in southeastern Ohio and western Pennsylvania, the reader is referred to the publications listed on page 10.



GENERALIZED SECTIONS SHOWING THE OIL AND GAS SANDS AND THE ACCOMPANYING BEDS IN THE AREAS FROM WHICH WATER AND ROCK SAMPLES WERE COLLECTED.

*A*, Woodsfield and Summerfield quadrangles, southeastern Ohio; *B*, Western Pennsylvania in region of Butler and Zelienople quadrangles.

*Generalized section of formations in eastern Ohio.*[a]

| System. | | Group or formation. | Thickness (feet). | Character. | Driller's description. |
|---|---|---|---|---|---|
| Carboniferous. | (Permian series.) | Washington formation. | 400 | Nonpersistent sandstone members with shale and clay of general reddish-brown color. A few thin beds of coal and limestone in lower portion. | |
| | (Pennsylvanian series.) | Monongahela formation. | 255-275 | Limestone, shale, and a little sandstone. Contains the Pittsburgh, Pomeroy, Meigs Creek, Uniontown, and Waynesburg coal beds, all of more or less value in the Woodsfield quadrangle. | |
| | | Conemaugh formation. | 460-475 | Irregular members grading into shales, commonly of reddish-brown or variegated colors. Upper and lower Pittsburgh limestone members near top; Ames and Cambridge limestone members a little below middle. Mahoning sandstone member at the base, locally productive of oil. | Includes First Cow Run, Buell Run, and Mahoning sands. |
| | | Allegheny formation. | 250-265 | Sandstone, shale, and important clay and coal beds, including the Lower Kittanning, Middle Kittanning, and Lower and Upper Freeport. | Includes Peeker, Macksburg 500-foot, and Second Cow Run oil sands named in descending order. |
| | | Pottsville formation. | 155-170 | Consists largely of sandstone and conglomerate, which rest with uneven contact on the eroded surface of the Mississippian beds. The sandstone is generally divided into several parts by beds of clay shale, and coals are also locally present. | Includes Maxton sand. |
| | | Unconformity | | | |
| | (Mississippian series.) | Maxville limestone. | 0-100 | Dark-gray and bluish to light-gray limestone with interbedded shale and fine-grained sandstone. | Big lime; includes Big lime sand. |
| | | Unconformity | | | |
| | | Logan formation. | 25-100 | Consists of sandstone, the Keener sand, interbedded with shale; a valuable source of oil and gas. | Includes Keener oil sand. |
| | | Black Hand formation. | 75-175 | Coarse sandstone interbedded with and grading laterally into sandy shale. | Probably includes Big Injun and Squaw oil sands. |
| | | Cuyahoga formation. | 350-450? | Mostly sandy shale in lower part, with a few beds of shaly sandstone. | Includes Welsh oil sand. |
| | | Sunbury shale. | 25-40 | Dark carbonaceous shale. | Black shale. |
| | | Berea sandstone. | 0-40 | Berea sand, consisting of coarse to fine grained gray to white sandstone. Lenticular in the Woodsfield and Summerfield quadrangles. | Berea oil and gas sand. |

---

[a] The part of this section below the Berea sandstone is taken from a paper by G. S. Rogers (The Cleveland gas field, Cuyahoga County, Ohio: U. S. Geol. Survey Bull. 661, p. 5, 1917).

*Generalized section of formations in eastern Ohio*—Continued.

| System. | Group or formation. | | Thickness (feet). | Character. | Driller's description. |
|---|---|---|---|---|---|
| Devonian or Carboniferous. | Bedford shale. | | 20-40 ? | Mottled gray, reddish, and brownish shale. | |
| Devonian. | Ohio shale group. | Cleveland shale. | 50-120 | Massive hard black bituminous, with a few bluish layers in lower portion. | Ohio shale, 1,100-3,000 feet, usually treated as a unit in southern Ohio. |
| | | Chagrin shale. | 850-1,200 | Soft bluish-gray clay shale, with some concretionary layers. | |
| | | Huron shale. | | Black and bluish shale in upper and lower portions, with a band of gray shale near middle. | |
| | Olentangy? shale. | | 80 | Gray calcareous shale. | |
| | Delaware limestone. | | 500-700 | Blue and gray limestone, becoming dolomitic in lower part. Contains a 30 to 50 foot bed of white quartz sandstone, 350 to 450 feet below top. | Big lime; includes Newburg sand and some "stray" sands in lower 300 feet, 490-1,825 feet. |
| | Columbus limestone. | | | | |
| Unconformity | Monroe formation. | | | | |
| Silurian. | Salina formation. | | 400-600 | Shale, dolomite, anhydrite or gypsum, and rock salt. | |
| | Niagara limestone. | | 400-600 | Dolomite and limestone. | |
| | "Clinton" formation. | | 150-250 | Crystalline limestone of various light colors; calcareous shale and thin-bedded limestone, with sandstone layer in lower part. | Includes Little lime, 75-150 feet. |
| | | | | | Clinton sand, 0-60 feet. |
| | | | | | 25-75 feet. |
| | "Medina" shale. | | 300-400 | Red clay shale, with thin layers of sandstone. | Medina red rock. |
| Ordovician. | Shale and limestone of Cincinnatian age. | | 750-1,250 | Dark shale, with thin layers of limestone, especially in upper part. | Slate and shells. |
| | Trenton (?) limestone. | | (?) | Limestone. | Trenton lime. |

## LITHOLOGY AND MINERALOGY OF THE SEDIMENTS.

### KINDS OF ROCK.

The reservoir rocks are principally porous ~~dolomitic limestones~~ and quartzitic and calcareous sandstones interbedded with relatively impermeable shales, tightly cemented sandstones, and gradations between these rocks. Fragments of the oil and gas bearing rocks were collected when they were cleaned from wells in the different fields and have been examined both petrographically and chemically.

### RESULTS OF PETROGRAPHIC EXAMINATION OF ROCK SPECIMENS.

For the petrographic study of the rock specimens we are indebted to M. I. Goldman, who reports as follows:

> The results of the petrographic study, presented herewith, are only tentative, as more detailed microscopic observations and more extensive study of the relation of the history and distribution of wells to the observed petrographic features are necessary to establish the conclusions.
>
> The primary object of the investigation was to find any characteristics of the rocks that might bear on the distribution of oil in them. As the work progressed it appeared that, in addition, light might be thrown on some of the early stages of metamorphism and their relation to geologic conditions. It was found impracticable to make determinations of pore space, because, by the tearing out of soft minerals and in other ways, holes are produced in grinding the thin sections. As methods for the determination of the primary or syngenetic features of sedimentary rocks from their thin sections are still rather undeveloped and inadequate, no attempt was made to determine those features beyond recognizing that quartz, feldspar, mica, and clay substance were the principal constituents of the rocks examined. Otherwise the investigation was limited to the study of secondary or epigenetic minerals.
>
> The following minerals were recognized:
>
> *Quartz* as a secondary growth around the original grains and in continuous crystallographic orientation with them was found in almost all the sandstones that were not too argillaceous. The approach to quartzite was in general greatest in the deepest beds, though this relation was highly variable.
>
> *Kaolinite*, known as a common mineral in sandstones, was found in fine crystalline aggregates filling the pore spaces.
>
> *Calcite* and other carbonates seemed to be particularly abundant in productive sandstones in older fields in which wells were very numerous, thus indicating a relation to recent ground-water circulation resulting from drilling.
>
> *Sulphides* (pyrite or marcasite) were scarce in oil and gas bearing rocks from the Woodsfield and Summerfield quadrangles and occurred mainly in the clays associated with carbonaceous matter, a common syngenetic relation. It is significant, however, as illustrating the mineralogic and chemical individuality of different fields, that in some regions outside of these areas in Ohio and Pennsylvania the sulphides are common in large aggregations in sandstones.
>
> *Chert and opal* growths were scarce and difficult to recognize and received no special attention.
>
> *Micas* are probably the most significant of the secondary minerals. They are of various species and types, from almost colorless to yellowish green and from brilliantly polarizing to almost isotropic. Their differentiation from syngenetic micas is difficult, being based mainly on habit and distribution. They are the minerals that most require further study, but so far as can be stated at present their development in the pay sands seems to be, like that of the carbonates, related to circulation of water resulting from the opening of wells. However, as is shown in the subsequent discussion by Messrs. Mills and Wells, the chemical changes that resulted in the formation of these secondary micas, like those that produced the carbonates and other epigenetic minerals, probably also took place during the slow natural circulation that preceded

drilling. In regard to changes in composition of the waters ~~associated with~~ oil and gas it is significant that some of the secondary micas ~~are evidently~~ chlorites and that magnesium would therefore have been used in forming them.

There were some indications that the development of secondary quartz and sulphides might also be related ~~to the circulation~~ of water resulting from the ~~removal of oil and gas.~~

An interesting feature is the apparent granulation and recementing by silica of some of the grains of quartz in a few of the samples. This may be the beginning of the mechanical part of metamorphism, but the possibility has also been suggested that it is due to crushing resulting from blows of the drill in sinking the well, with subsequent cementing. A choice between these two interpretations could be made only on the basis of a study of the distribution of the samples showing this feature. The assumption of metamorphism due to pressure resulting from the weight of overlying beds is favored by the two facts that the phenomenon is apparently rare and that, so far as may be concluded from this preliminary study, it occurs mainly in samples from greater depths, especially in one from a depth of 2,230 feet.

No determinations of possible water-soluble minerals in the sections could be made, as these would be removed in grinding.

It may be noticed that all the factors considered above are related to the occurrence and circulation of underground waters in the rocks. The underground waters in turn, as shown elsewhere in this paper, have important bearings on the occurrence of oil and gas.

A dark-brown stain, believed to be due to oil, is found in connection with carbonaceous matter in some of the clays, a relation well recognized in the oil shales of the western United States.[1] No other direct relation between the oil and gas associated with the rocks and their microscopic features was established. The porosity would of course be one of the most important properties to consider if the conditions under which thin sections are produced permitted its determination under the microscope.

As regards metamorphism ~~in general, it is suggested~~ that at least during the earliest stages ~~an important~~ factor ~~may be~~ the presence of open fissures or passages of exceptional porosity which would facilitate the flow of water through the rocks.

### RESULTS OF CHEMICAL EXAMINATION OF ROCK SPECIMENS.

In order to supplement the microscopic examination of the rock specimens obtained from the oil and gas wells, a number of chemical determinations were made, together with a few fairly complete analyses. The proportions of the water-soluble constituents were first determined by extracting 2-gram portions of the powdered samples with about 100 cubic centimeters of water at ordinary temperature, filtering, evaporating the filtrates to dryness at 110° C., and weighing the residues. In Table 1 the results are stated as percentages of the rocks "soluble in water." The composition of the water-soluble material was not ascertained in the first determinations, but it is believed to have been largely sodium chloride, as indicated in Tables 3 and 15. The proportion of water-soluble materials ranged from 0.25 to 0.84 per cent. Next the leached portions of the samples were extracted with 1/10 hydrochloric acid in order to gain an insight into the nature of the acid-soluble constituents. The results are stated as percentages of the rock "soluble in HCl." After this treatment the residue was extracted with 5 per cent solution of sodium carbonate to determine the amount of soluble silica present.

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[1] See the studies of the late C. A. Davis.

TABLE 1.—*Chemical determinations on rock specimens from oil and gas wells.*

[Percentages of samples by weight. Determinations by R. C. Wells.]

| | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Soluble in water[a] | 0.05 | 0.17 | 0.35 | 0.84 | 0.57 | 0.10 |
| Soluble in 1/10 HCl: | | | | | | |
| $SiO_2$ | .29 | .97 | .12 | .10 | .04 | .08 |
| $Fe_2O_3$[b] | .95 | 4.75 | 2.35 | 1.13 | .11 | .68 |
| $Al_2O_3$ | .33 | 1.47 | .32 | .14 | .03 | .09 |
| CaO | .12 | .37 | 2.72 | 1.35 | .08 | .19 |
| MgO | .08 | .56 | .73 | .37 | None. | .09 |
| $P_2O_5$ | .02 | .10 | .03 | .01 | .02 | Trace. |
| $CO_2$ | Trace. | 2.14 | 4.23 | 1.80 | None. | Trace. |
| Soluble in 5 per cent solution of $Na_2CO_3$: | | | | | | |
| $SiO_2$ | .15 | .63 | .14 | .18 | .07 | .17 |

[a] Mainly chlorides.

[b] All Fe as $Fe_2O_3$.

1. Keener sand, of late Mississippian age; depth 1,451 to 1,469 feet; Jerusalem, Sunsbury Township, Monroe County, Ohio. Fragments of sandstone had been shot and cleaned from an old oil well and had lain exposed to the weather for several months before being collected.
2. Shale underlying Third sand, of probable late Devonian age; depth, 1,450± feet; Evans City, Butler County, Pa. Fragments of shale drilled from a new well and collected at once.
3. Berea sand, of early Mississippian age; Armstrongs Mills, Washington township, Belmont County, Ohio. Fragments of sandstone cleaned from a gas and oil well 10 years old. The sample was collected as soon as it was removed from the well.
4. Berea sand, of early Mississippian age; depth, 1,900± feet; Woodsfield, Center Township, Monroe County, Ohio. Fragments of sandstone cleaned from a gas and oil well 10 years old. The sample was collected as soon as it was removed from the well.
5. Big lime sand (sandy phase of Maxville limestone), of late Mississippian age; depth, 1,400± feet; Ozark, Sunsbury Township, Monroe County, Ohio. Fragments of sandstone shot and cleaned from a new oil well in an old field. The sample was collected as soon as it was removed from the well.
6. Third sand, of probable late Devonian age; depth 1,430 to 1,460 feet; Evans City, Forward Township, Butler County, Pa. Fragments of sandstone shot and cleaned from a new oil well in a new field. The sample was collected as soon as it was cleaned from the well.

In Table 2 are presented the results of the more complete analyses.

TABLE 2.—*Analysis of rock specimens from oil and gas wells.*

[R. C. Wells, analyst.]

| | 1 | 2 | 3 |
|---|---|---|---|
| $SiO_2$ | 93.82 | 62.17 | 85.90 |
| $Fe_2O_3$ (all Fe as $Fe_2O_3$) | 1.75 | 7.54 | 2.82 |
| $Al_2O_3$ | .73 | 16.84 | 1.68 |
| CaO | .19 | .44 | 2.96 |
| MgO | .25 | 1.46 | .84 |
| $P_2O_5$ | .02 | .10 | .03 |
| $CO_2$ | Trace. | 2.14 | 4.23 |
| $TiO_2$ | .12 | .87 | .12 |
| Loss on ignition, less $CO_2$ | 2.31 | 3.95 | 1.35 |
| | 99.19 | 95.51 | 99.93 |

1. Keener sand, of late Mississippian age; depth, 1,451 to 1,469 feet; Jerusalem, Sunsbury Township, Monroe County, Ohio. Fragments of sandstone had been shot and cleaned from an old oil well and had lain exposed to the weather for several months before being collected.
2. Shale underlying Third sand, of probable late Devonian age; depth, 1,450± feet; Evans City, Butler County, Pa. Fragments of shale drilled from a new well and collected at once.
3. Berea sand, of early Mississippian age; Armstrongs Mills, Washington Township, Belmont County, Ohio. Fragments of sandstone cleaned from a gas and oil well 10 years old. The sample was collected as soon as it was removed from the well.

The chemical tests were made partly to ascertain the character of the cementing material. That generally found in sandy sediments includes silica and hydrous silicates of iron, aluminum, calcium, and magnesium, the composition depending somewhat on the foreign substances in the sand. As a matter of fact, pure siliceous sandstones are the exception. When, as in the rocks examined, clay, mud, and carbonates are also present the list of possible cements is greatly increased and includes the carbonates of iron, magnesium, and calcium and various phosphates and sulphates.

Tables 1 and 2 show that the proportion of carbonates in the sands examined is not large; in fact, carbonates are absent in the Bib lime sand, and only traces are found in the specimens of the Keener and Third sands. Much of the iron found in the shale below the Third sand and in the Berea sand from Woodsfield and practically all of that in the Berea sand from Armstrongs Mills is present as ferrous carbonate, although reported as ferric oxide; the determination of ferrous iron is unreliable in the presence of organic matter. Magnesium was found in all but one of the sands, and some calcium in all. Sands 2, 3, and 4 effervesce with acid, but the other three sands show no appreciable effervescence. Sample 4, collected from an old well yielding oil and gas from the Berea sand, is salty to the taste and shows the largest proportion of material soluble in water. None of the specimens shows a marked amount of silica soluble in acid or in sodium carbonate after treatment with acid, except the shale below the Third sand. This rock may contain a magnesium silicate which is decomposed by acid. The magnesium content of all the specimens appears to be low, though it must be remarked that the relatively insoluble magnesium silicates would not be dissolved under the conditions of these experiments. Dolomite is present only in small amounts, but specimens of the deeply buried limestones that have been previously reported as dolomitic could not be procured for examination.

Small proportions of water-soluble salts, more particularly sodium chloride, were found in all the rock samples in which these constituents were sought. Some uncertainty as to the mode of occurrence of the salts is introduced by the small proportions contained in the rocks examined. The salts are present in smaller proportions than would be found in a sandstone having a total porosity of 15 per cent if it were saturated with an average Appalachian oil field brine and then dried. It may therefore be suggested that the salts in the specimens examined have been deposited merely by the drying of small amounts of brine contained in the rocks when the specimens were collected. This suggestion would be reasonable if the rocks had been saturated with water when they were collected from the wells, but some of them were partly saturated with oil and came from relatively water-dry strata. ~~The occurrence in a sedimentary rock, now relatively dry of water, of 0.5 per cent of water-soluble matter, of~~ which 82.7 per cent ~~is made up of chlorides,~~ suggests that salts of this type were deposited in the rock as a result of deep-seated ~~evaporation.~~

As will be explained later, the brines associated with oil and gas in the Appalachian fields have probably undergone concentration, and the salt that occurs in densely cemented barren rock may have been included in other minerals deposited chemically from the waters before they reached their present stage of concentration. In other words, water concentration and cementation have probably been more or less concomitant processes, and the soluble salts, especially sodium chloride, may have been mechanically included in the cements. It is significant that chlorides, especially sodium chloride, occur in the densely cemented sediments and in secondary deposits of calcite and barite collected from oil wells. The possibility that the included sodium chloride was formed concomitantly with calcium carbonate by the mixing and concentration of waters of different types is discussed in the succeeding text. As related to the concentration problem, which is also developed in succeeding pages, it seems important that sodium chloride constitutes 86.5 to 100 per cent of the chlorides present in the samples examined, whereas the salts obtained by the complete evaporation of the brines contain about 20 per cent of calcium chloride and 5 per cent of magnesium chloride.

TABLE 3.—*Water-soluble material, chlorides, and sodium chloride in deeply buried sediments.*

[S. C. Dinsmore, analyst.]

| | Percentage of water-soluble material in the rocks. | Percentage of chlorides in the rocks. | Percentage of NaCl in the rocks. | Percentage of NaCl in the chlorides. |
|---|---|---|---|---|
| 1 | 0.131 | 0.029 | 0.029 | 100.0 |
| 2 | .245 | .157 | .150 | 95.5 |
| 3 | .332 | .173 | .165 | 95.4 |
| 4 | .139 | .098 | .096 | 98.0 |
| 5 | .509 | .421 | .364 | 86.5 |
| 6 | .092 | .043 | .043 | 100.0 |

1. Densely cemented siliceous shale underlying Third sand; depth 1,450± feet; Evans City, Butler County, Pa. The shale appeared to be relatively dry of salt water and oil.
2. Hundred-foot sand; depth 1,060± feet; Evans City, Butler County, Pa. The sample was cleaned from the productive horizon in a new oil well in an old field. The well yielded both oil and salt water.
3. Berea sand; Armstrongs Mills, Belmont County, Ohio. Cleaned from an old oil well.
4. Third sand; depth 1,422 feet; near Evans City, Butler County, Pa. The sample was cleaned from a new oil well. The sand yielded oil but was reported to be relatively free from salt water.
5. Big lime sand; depth 1,400± feet; half a mile west of Ozark Village, Sunsbury Township, Monroe County, Ohio. The sample was cleaned from a new oil well in an old field where the Big lime sand is reported to be relatively dry of salt water.
6. Hundred-foot sand; Jefferson Township, Butler County, Pa. Cleaned from a new well in which gas, oil, and water were practically absent.

The analyses on which Table 3 is based were made in the following manner:

A 50-gram portion of the finely pulverized sample was leached with 300 cubic centimeters of distilled water at 45° C. for 17 hours, with frequent stirring. The resultant solution was then filtered into a graduated 500 cubic centimeter flask and the leached sample washed with distilled water until the filtrate attained a volume of 500 cubic centimeters. Aliquot portions, representing 10 grams of the sample, were taken for determinations of total water-soluble material, Ca, Mg, Na, K, $SO_4$, and Cl. The material that was soluble in water was determined by evaporating to dryness and heating at 110° C. for one hour, cooling the residue in a desiccator, and weighing. Other analytical determinations were made in the usual manner.

## RESULTS OF PHYSICAL EXAMINATION OF ROCK SPECIMENS.

In order to study further the character of these rocks, physical tests were made on lump specimens to determine the percentage of total pore space in which oil, gas, and water might occur or in which mineral matter might be deposited. For this work we are indebted to A. F. Melcher, of the United States Geological Survey. The total proportions of pore space in the fragments tested are shown in Table 4 to range from 4 or 5 up to 18 or 19 per cent of the rock volume. Notwithstanding the care exercised in collecting the specimens, some of the lumps of rock that are thought to be pay sand, which were obtained after productive oil and gas wells had been shot, may represent hard, relatively dense layers of the sandstone and not the porous, open-textured pay sands from which the oil and gas are derived. Apparently no consistent relation exists between the porosity of the sands and the size and shape of the component grains. The variations in porosity are due largely to the irregularity with which the sediments have been cemented both before and during the extraction of oil and gas.

In addition to the porosities shown in Table 4 Richardson[1] reports that some lump samples of the Hundred-foot sand collected in Butler County, Pa., have total porosities as low as 4.5 to 7.3 per cent. It seems probable that the total pore space in the relatively open-textured parts of the Hundred-foot sand may be at least 15 to 18 per cent or more of the rock volume, though we have no positive data on this subject.

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[1] Richardson, G. B., Note on Appalachian oil field brines: Econ. Geology, vol. 12, pp. 39–41, 1917.

TABLE 4.—*Total pore space in oil and gas bearing sands and associated rocks, with diameter and density of the component grains.*[a]

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | | | 11 | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Total weight of sample, grams | 53.2390<br>31.9740 | 10.7327 | 17.7060 | 40.8190 | 41.1200 | 8.9700 | 16.2382 | 14.0895 | 5.7653 | 41.4818 | 19.6930 | 8.4463 | 28.5912 | 5.0573<br>4.3093 | 3.8192 | 1.9555 | 36.4121<br>28.8998 | 60.8670<br>43.2127<br>30.9790 |
| Pore space ........per cent | 11.2<br>10.8 | 7.0 | 12.7 | 12.7 | 13.1 | 11.3 | 4.7 | 9.7 | 11.0 | 17.7 | 14.5 | 18.4 | 10.5 | 11.0<br>12.4 | 13.0 | 11.3 | 14.7<br>15.0 | 17.1<br>15.9<br>17.4 |
| Total weight sieved, grams | 7.955 | 5.400 | 6.435 | 13.125 | 10.925 | 8.940 | 7.635 | 6.450 | 3.625 | 6.940 | 6.970 | 6.245 | 8.535 | 5.060 | 2.520 | 1.930 | 9.220 | 11.465 |
| Diameter (millimeters): | | | | | | | | | | | | | | | | | | |
| More than 1.65..per cent | ........ | ........ | ........ | ........ | 20.4 | 0.6 | ........ | ........ | 0.8 | 1.9 | 23.5 | 0.2 | ........ | ........ | ........ | ........ | ........ | ........ |
| 1.651–0.833 ........do | ........ | ........ | ........ | ........ | 56.4 | 31.8 | ........ | ........ | .8 | 41.1 | 34.4 | 2.6 | ........ | ........ | 8.5 | ........ | ........ | ........ |
| 0.833–0.417 ........do | ........ | ........ | ........ | ........ | 14.7 | 45.2 | ........ | ........ | 16.6 | 47.2 | 30.1 | 78.9 | ........ | ........ | 70.8 | ........ | ........ | ........ |
| 0.417–0.295 ........do | ........ | ........ | ........ | 2.4 | 2.5 | 10.3 | ........ | ........ | 18.3 | 3.4 | 5.1 | 12.4 | 4.6 | ........ | 12.9 | 30.3 | ........ | 0.3 |
| 0.295–0.208 ........do | ........ | 8.3 | ........ | 29.4 | 1.7 | 5.0 | ........ | ........ | 13.8 | 2.7 | 3.6 | 2.6 | 29.6 | ........ | 3.2 | 28.8 | ........ | 25.4 |
| 0.208–0.147 ........do | 48.0 | 50.6 | 13.1 | 53.3 | 1.6 | 3.6 | 36.0 | ........ | 11.2 | 1.7 | 1.7 | 1.4 | 30.1 | 18.7 | 1.4 | 20.5 | 0.4 | 54.3 |
| 0.147–0.104 ........do | 36.8 | 26.1 | 63.3 | 10.1 | 1.1 | 1.7 | 38.2 | 37.6 | 11.0 | 1.0 | .9 | .9 | 10.0 | 48.6 | 1.0 | 10.1 | 56.8 | 11.4 |
| 0.104–0.074 ........do | 4.9 | 3.7 | 8.6 | 1.7 | .7 | .4 | 9.6 | 26.0 | 12.0 | .5 | .4 | .4 | 10.3 | 12.6 | .4 | 4.1 | 20.0 | 2.9 |
| 0.074–0.000 ........do | 10.3 | 11.3 | 15.0 | 3.2 | .9 | 1.2 | 16.2 | 36.4 | 15.4 | .6 | .3 | .6 | 15.5 | 20.1 | 1.8 | 6.2 | 22.8 | 5.8 |
| | 100.0 | 100.0 | 100.0 | 100.1 | 100.0 | 99.8 | 100.0 | 100.0 | 99.9 | 100.1 | 100.0 | 100.0 | 100.1 | 100.0 | 100.0 | 100.0 | 100.0 | 100.1 |
| Density of sand grains | 2.647 | 2.675 | 2.659 | 2.646 | 2.654 | 2.651 | 2.665 | 2.727 | 2.705 | 2.653 | 2.649 | 2.647 | 2.649 | 2.662 | 2.751 | 2.658 | 2.698 | 2.682 |

[a] The rock specimens upon which these tests were made were collected by D. Dale Condit and R. Van A. Mills in or near the Woodsfield and Summerfield quadrangles in southeastern Ohio. The physical determinations were made by A. F. Melcher.

1. Berea sand; depth 2,050± feet; Woodsfield, Center Township, Monroe County, Ohio. Fragment from a productive oil well.

2. Berea sand; depth 1,807–1,829 feet; Woodsfield, Center Township, Monroe County, Ohio. Hard, densely cemented fragment from a Berea gas well.

3. Berea sand; depth 1,440± feet; sec. 26, Buffalo Township, Noble County, Ohio. Hard, densely cemented fragment from a nonproductive well.

4. Keener sand; depth 1,539–1,570 feet; Woodsfield, Center Township, Monroe County, Ohio. From the bed which yielded gas, oil, and salt water.

5. Big Injun sand; depth 1,460–1,470± feet; Lewisville, Summit Township, Monroe County, Ohio. From the bed which yielded gas, oil, and salt water. The initial daily yield from the well was 80 barrels of oil.

6. Keener sand; depth 1,220–1,259 feet; Coats Station, Center Township, Monroe County, Ohio. Fragment of sandstone from the bed from which oil and salt water were pumped.

7. Berea sand; depth 1,535± feet; Chaseville, Seneca Township, Noble County, Ohio. Hard, densely cemented fragment from a nonproductive well.

8. Hard, bluish-gray shale overlying the Keener sand; depth 1,445± feet; Jerusalem, Sunsbury Township, Monroe County, Ohio.

9. Light bluish-gray shale underlying the Keener sand; depth 1,475± feet; Miltonsburg, Malaga Township, Monroe County, Ohio.

10. Keener sand; depth 1,451–1,469 feet; Jerusalem, Sunsbury Township, Monroe County, Ohio. Loosely cemented sandstone from productive bed. The initial daily production of oil from the well where this sample was collected was approximately 400 barrels.

11. Berea sand; depth 1,890–1,920± feet; Woodsfield, Center Township, Monroe County, Ohio. Fragment from productive bed. The well from which this sample was collected yielded both gas and oil.

12. Berea sand; depth 1,500± feet; Chaseville, Seneca Township, Noble County, Ohio. Fragment from productive bed. The well from which the sample was collected yielded oil and gas with practically no salt water.

13. Gas sand; depth 1,350–1,355 feet; sec. 11, Malaga Township, Monroe County, Ohio. Fragment from a bed that yielded gas.

14. Big Injun sand; depth 1,460–1,500± feet; Lewisville, Summit Township, Monroe County, Ohio. Fragment from a bed that yielded oil and salt water.

15. Berea sand; depth 2,140–2,160± feet; Woodsfield, Center Township, Monroe County, Ohio. Fragment from productive bed. The well from which the sample was collected yielded oil with very little salt water.

16. Berea sand; Armstrongs Mills, Belmont County, Ohio. Fragment from productive bed.

## CHARACTERISTICS OF THE OIL AND GAS IN THE APPALACHIAN FIELDS.

The chemical examination by the Bureau of Mines of crude petroleum and natural gas collected during our field studies and the many other available analyses of the oils and gases from the areas studied[1] indicate that the oils are composed essentially of members of the paraffin series and contain no asphalt. It is evident from their generally low specific gravity, ranging from 0.6837 to 0.8482, and also from their fractional distillation, especially between 150° and 300° C., that the oils, with but few possible exceptions, contain no considerable proportions of the aromatic series. The sulphur content of the oils is also insignificant.

Analyses of natural gas from the Appalachian fields, reported in percentages by volume, moisture free, show that the gas consists essentially of the paraffin hydrocarbons methane and ethane. The usual methane content ranges from 66.0 to 98.0 per cent and that of ethane from less than 1 to more than 29 per cent. The carbon dioxide content ranges from less than 0.1 to more than 5 per cent; and that of nitrogen from less than 0.5 to more than 5 per cent. The oxygen content is generally less than 0.5 per cent. The proportions of hydrogen sulphide and other minor constituents are practically negligible.

It is unfortunate that little or no attention has been paid to the accurate determination of the moisture content of natural gas as it is drawn from the reservoir rocks and that inadequate study has been given to the physical and chemical relations existing between petroleum and natural gas on the one hand and their associated waters and reservoir rocks on the other.

## OCCURRENCE AND DISTRIBUTION OF WATER IN THE STRATA.

### PRESENT DISTRIBUTION OF WATER IN THE OIL AND GAS BEARING ROCKS.

#### WATER-BEARING SANDS.

In the Appalachian fields the oil sands of both the Pennsylvanian and Mississippian series are generally water bearing throughout, though some of the beds are locally termed dry because they do not yield perceptible flows of water into open wells. Thus in the Woodsfield and Summerfield quadrangles, in southeastern Ohio, the Big lime sand, a lenticular sandstone in the Maxville limestone, of late

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[1] Day, D. T., The production of petroleum in 1913: U. S. Geol. Survey Mineral Resources, 1913, pt. 2, pp. 1126–1284, 1914.

Mississippian age, is locally termed dry, though in places within these quadrangles, it is characteristically water bearing. The Keener and Big Injun sands in southeastern Ohio are characteristically water bearing, though they too fail to yield appreciable flows of water in certain oil and gas fields and in some barren areas. In general wherever in western Pennsylvania paying quantities of oil are found in the ~~Hundred-foot sand, of probable early Mississippian~~ age, that sand contains abundant water.

### DRY SANDS.

Some of the oil and gas bearing sands are relatively free from water—that is, they fail to yield perceptible flows of water into open wells and are consequently termed dry sands. In some of the beds of the Devonian system or of probable Devonian age, more particularly those of the Catskill (?) formation in western Pennsylvania, the apparent absence of water is the rule rather than the exception. Here again, however, the distribution of water is irregular, parts of the so-called dry sands evidently being saturated with water.

We believe that in strata penetrated by the drill the existence of a sand actually dry of water is doubtful. The occurrence of small amounts of water in a sand may be overlooked because the water evaporates into gas entering wells, or because the proportion of water accompanying oil may be too small to be observed. Water is generally found at the bottoms of inclosed or covered field tanks that receive oil from so-called dry sands. Such sands are only relatively dry of water. The failure of a bed to yield a perceptible flow of gas, oil, or water into a well does not necessarily signify the absence of any of these fluids. In beds such as shales and tight sands the rock interstices may be too fine to emit noticeable amounts of the fluids, or the fluid movements into a well may be so slow as to require several days or even weeks to make the presence of gas, oil, or water noticeable. The fact that water introduced into a well is absorbed by a sand indicates merely the comparative dryness of that sand but in no way signifies the absence of water.

Several explanations have been offered to account for the so-called dry sands. In a recent contribution Reeves[1] concludes that the "non water-bearing" sandstones of what has been called the Catskill formation in southwestern Pennsylvania and West Virginia were dried out while exposed to the air under the semiarid conditions which he supposes to have existed during the Catskill time. He further postulates the exclusion of water from these beds during later submergence, owing to the presence of interstitially included air.

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[1] Reeves, Frank, The absence of water in certain sandstones of the Appalachian oil fields: Econ. Geology, vol. 12, pp. 354–378, 1917.

The abundance of epigenetic minerals with which the so-called dry sands are cemented and which were evidently deposited from circulating water suggests to us the long-continued presence of more water than the so-called dry sands now contain. What therefore seems to be a more plausible explanation for the comparative dryness of certain beds is that the displacement of water in these beds by compacting and cementation or by the incursion of petroleum and natural gas [1] has been relatively complete, or that the sands may have been partly dried out by the evaporative processes herein described. In regard to this last suggestion, it is a significant fact that the water content of the strata decreases and that the degree of concentration of the dissolved constituents of the waters increases with increasing depth.

An argument used by Reeves, that red beds are proof of the former existence of an arid climate, is somewhat weakened by the fact that red ferric oxide may be formed from hydrated ferric oxide by the dehydrating action of salt solutions, just as anhydrite is similarly formed from gypsum. Daubrée[2] states that he carried out this dehydration experimentally in a saturated solution of sodium chloride at only 150° C. According to him, Élie de Beaumont[3] seems to have been the first to point out the causal relation between salt formations and the variegated red tint of certain clays, sandstones, and even of salt itself.

In showing that water does not always disappear at depth, Reeves[4] calls attention to the occurrence of salt water in the Lower Devonian rocks near Charleston, W. Va., and McDonald, Pa. In a deep well at McDonald, salt water was encountered at a depth of 6,260 feet, presumably in the Oriskany sandstone, and rose 4,000 feet in the well. During the preparation of this bulletin we have collected and examined waters from the Upper Devonian series in Butler County, Pa., where the beds in many places are termed dry.

Broadly speaking, we believe that within the Appalachian basin all the sands reached by the drill are water bearing and that there is no regional level of water saturation above which a deeply buried oil and gas bearing rock is dry. The so-called water surfaces, the upper limits of water saturation, and the so-called non water-bearing portions of the oil and gas bearing sands are only local in their occurrence.

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[1] Johnson, R. H., The rôle and fate of the connate water in oil and gas sands: Am. Inst. Min. Eng. Trans., vol. 51, pp. 587–592, 1916.

[2] Études et expériences synthétiques sur le metamorphisme: Annales des mines, 5th ser., vol. 16, p. 411, 1859; Smithsonian Inst. Ann. Rept., 1861, p. 270.

[3] Daubrée's reference is "Explication de la carte géologique de France, vol. 2, p. 94."

[4] Reeves, Frank, The absence of water in certain sandstones of the Appalachian oil fields: Econ. Geology, vol. 12, pp. 354–378, 1917.

The irregular distribution and arrangement of the gas, oil, and water contents of the productive sands are due, no doubt, to a complex succession of events in which rock movements, the displacement of water by oil and gas, compacting and cementation of the sediments, conditions of structure, texture, and lenticularity of the beds, the evaporation of water into moving and expanding gases, and, finally, the movements of the fluids incident to gas and oil extraction by man have afforded important modifying conditions.

Surface waters are constantly percolating into the shallow rocks, so that near the surface and near the outcrops of the reservoir rocks the saline waters undergo dilution by incursions of water from shallower sources. The distribution of typical Appalachian oil-field brines, having only chloride salinity, is therefore limited to those beds in which the excessive influx of surface water has been prevented.

## MODE OF OCCURRENCE OF PETROLEUM, NATURAL GAS, AND WATER IN THE WATER-BEARING SANDS.

### OIL, GAS, AND WATER MIXTURES.

In order to explain more clearly the changes that the waters associated with petroleum and natural gas undergo during the extraction of these substances from their reservoir rocks, it is necessary to consider the mode of occurrence. A fact that seems to have been generally overlooked is that in most of the water-saturated pay sands in the Appalachian fields the natural segregation of gas and oil above water is very incomplete, so that gas, oil, and water occur intimately mixed in the interstices of the pay sands. Munn[1] has described this mode of occurrence of petroleum in the Sewickley quadrangle, in Pennsylvania, where portions of the Hundred-foot sand were inferred by him to be completely saturated with mixtures of oil and water. Field observations supplemented by inquiries among operators in the Butler and Zelienople quadrangles, in western Pennsylvania, have led to the conclusion that similar mixtures occur in the Hundred-foot sand throughout these two quadrangles. A more thorough investigation in the Woodsfield and Summerfield quadrangles, in southeastern Ohio, affords convincing evidence that this is a common mode of occurrence of both gas and oil in the water-saturated sands in these areas. This mode of occurrence of mixtures of gas, oil, and water involves a very indefinite demarcation between water and overlying mixtures rich in the hydrocarbons, the so-called oil-water surfaces being extremely irregular gradations from mixtures containing large proportions of oil and gas to mixtures less rich in these substances or to water containing too little gas and oil to warrant production. Where the top of a typical water-bearing pay sand is relatively high, owing to folding or to the lenticular character of the sand, gas and oil are frequently found more completely segregated above the water than in the adjacent portions of the same sand where the mixtures are less rich in gas and oil.

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[1] Munn, M. J., Geology of the oil and gas fields in the Sewickley quadrangle, Pa.: Pennsylvania Top. and Geol. Survey Comm. Rept. 1, p. 85, 1910.

Another important fact, brought forth by these detailed studies, is that the so-called oil-water surfaces, the irregular and indefinite contacts between oil and water, appear from well logs to be inclined in the same direction as the tops of the pay sands, though less steeply. Such inclined oil-water surfaces in Oklahoma have been described by Beal.[1]

## EVIDENCE OF THE OCCURRENCE OF OIL, GAS, AND WATER MIXTURES.

Evidence bearing upon the conditions above set forth has been procured by inquiries among oil and gas men, together with detailed observations in the different fields that we have studied. Gas, oil, and water are generally produced simultaneously from wells drilled either to the tops of water-saturated pay sands or only a few feet into them. Many of these wells continue to produce mixtures of oil and water together with gas for periods of 10 to 30 years. Some of them flow at first several hundreds or thousands of barrels of mixed oil and water a day. Those that originally yield large quantities of oil with practically no water generally yield both water and oil as the initial rates of flow diminish. These phenomena are due partly to the differential flow of oil and water through the sands, but it is not probable that great volumes of oil, gas, and water would be yielded together from the top of a pay sand just tapped if the segregation of the gas and oil above the water were at all complete.

In several fields it has been possible to compare the yields from individual wells that were first drilled to the tops of the pay sands and were subsequently drilled deeper into the same pays. For example, a well near Miltonsburg, Malaga Township, Monroe County, Ohio, was first drilled 3 feet into the Keener sand in November, 1915, and had an initial daily rate of production of 9 barrels of oil with 12 barrels of salt water. After having been pumped for three months the well was yielding only 3½ barrels of oil a day, though the daily production of water remained at about 12 barrels. In April, 1916, the daily rate of oil production had declined still further, though the water production remained about the same. The well was then drilled 6 feet deeper into the pay sand and yielded 7 barrels of oil a day, with about 18 barrels of salt water. If at this place the segregation of oil above the water had been nearly complete, the increase in depth of the well would probably have brought about a relatively large increase in the amount of water produced and a correspondingly small increase in the amount of oil. On the contrary, however, the production of oil was increased 100 per cent by drilling the well deeper, whereas the production of water was increased only 50 per cent. The oil and water must have been rather intimately mixed, a large proportion of the oil occurring below the water that was being produced before the well was deepened.

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[1] Beal, C. H., Geologic structure in the Cushing oil and gas field, Okla., and its relation to the oil, gas, and water: U. S. Geol. Survey Bull. 658, 1917.

The example cited is typical of a large number of such occurrences reported during our field studies. It must be noted, however, that drilling wells deeper in water-saturated sands is dangerous, because of the large amounts of water that may be encountered under the rich oil and water mixtures in the same or underlying pay sands. Many valuable wells have been spoiled in this way.

## TEMPERATURE AND PRESSURE.

The temperatures at which oil, gas, and water occur in their reservoir rocks were not measured during our field investigations but are shown by the deep-well temperature measurements of Hallock,[1] Johnston,[2] and Van Orstrand[3] to range from 18° or 19° C. at a depth of 1,000 feet to about 33° to 36° C. at a depth of 3,000 feet. To what extent the rocks together with their included waters and hydrocarbons have cooled subsequent to periods of regional deformation or subsequent to periods of deepest burial is of course uncertain, but it is reasonable to assume that the waters under scrutiny have been subjected to much higher temperatures than those just quoted. Such a supposition is strengthened by the occurrence of highly heated saline waters in the oil fields of Louisiana and Texas.

Data relative to initial gas pressures encountered in various reservoir rocks were furnished by operators. These pressures range from only a few pounds to the square inch in the shallow sands to several hundred pounds in the deeper beds. In the Woodsfield and Summerfield quadrangles the initial gas pressures may be summarized as follows: Big lime sand, 400 to 440 pounds to the square inch; Keener sand, 470 to 480 pounds; Big Injun sand, 500 pounds; Berea sand, 565 to 735 pounds. In the Butler and Zelienople quadrangles the following initial gas pressures in the deeper sands are reported: Hundred-foot sand, 750 to 810 pounds to the square inch; Third sand, 750 to 820 pounds; Fourth sand, 810 to 930 pounds, and Fifth sand, 860 to 875 pounds.

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[1] Hallock, William, Subterranean temperatures at Wheeling, W. Va., and Pittsburgh, Pa.: School of Mines Quart., vol. 18, pp. 148–153, 1897.

[2] Johnston, John, Note on the temperature in the deep boring at Findlay, Ohio: Am. Jour. Sci., 4th ser., vol. 36, pp. 131–133, 1913.

[3] Van Orstrand, C. E., unpublished manuscript, U. S. Geological Survey.

The following table contains some data from the literature and from our unpublished notes on gas pressures:

TABLE 5.—*Initial gas pressures at different depths in several gas fields.*

| Name of bed. | Locality. | Depth (feet). | Initial gas pressure (pounds per square inch). | Average increase of pressure per 100 feet (pounds per square inch). | Authority. |
|---|---|---|---|---|---|
| Salt sand | Woodsfield, Ohio | 1,295 | 280 | 22 | Authors' notes: Data furnished by various oil and gas companies. |
| Big lime sand | Southwest corner of Wayne Township, Belmont County, Ohio. | 1,310 | 365 | 28 | Do. |
| Do | Southeast corner of Malaga Township, Monroe County, Ohio. | 1,412 | 400 | 28 | Do. |
| Do | Wayne Township, Belmont County, Ohio. | 1,465 | 440 | 30 | Do. |
| Keener sand | Woodsfield, Ohio | 1,515 | 475 | 31 | Do. |
| Big Injun sand | do | 1,468 | 500 | 34 | Do. |
| Berea sand | do | 2,090 | 710 | 34 | Do. |
| Do | Summerfield, Ohio | 1,698 | 565 | 33 | Do. |
| Do | Sunsbury Township, Monroe County, Ohio. | 2,060 | 735 | 36 | Do. |
| Butler gas sand | Summit Township, Butler County, Pa. | 1,200 | 380 | 32 | Do. |
| Hundred-foot sand | Butler, Pa | 1,400 | 780 | 56 | Do. |
| Third sand | do | 1,700 | 785 | 46 | Do. |
| Do | do | 1,452 | 600 | 41 | Do. |
| Fourth sand | do | 1,800 | 870 | 48 | Do. |
| Do | do | 1,568 | 225 | 14 | Do. |
| Fifth sand | do | 1,950 | 870 | 45 | Do. |
| "Clinton" sand | Harrison Township, Knox County, Ohio. | 2,700 | 810 | 30 | Do. |
| Do | Cleveland, Ohio | 2,500<br>2,900 | 800<br>1,100 | 32-38 | Rogers.[a] |
| Do | Newberg, Ohio | 3,000 | 425 | 14 | Van Horn.[b] |
| 'Trenton" limestone | Findlay, Ohio | 950 | 400-450 | 42-47 | Orton.[c] |
| Do | Kokomo, Ind | 650 | 328 | 50 | Do. |
| Do | Cleveland, Ohio | 4,500 | 37 | 0.82 | Van Horn.[b] |
| Benson sand | Barbour County, W. Va. | 4,090 | 1,800 | 44 | I. C. White.[d] |
| (?) | West Virginia | 2,989 | 1,420 | 47 | Do. |
| (?) | Havre, Mont | 947 | 490 | 52 | Stebinger.[e] |
| (?) | do | 1,370 | 540 | 39 | Do. |
| (?) | Louisiana | 1,650 | 650 | 39 | Knapp.[f] |
| Unconsolidated sand | do | 1,800 | 600 | 33 | Do.[g] |
| (?) | Loco, Okla | 750 | 310 | 41 | McMurray and Lewis.[h] |

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[a] Rogers, G. S., The Cleveland gas field, Cuyahoga County, Ohio: U. S. Geol. Survey Bull. 661, p. 37, 1917.

[b] Van Horn, F. R., Reservoir gas and oil in the vicinity of Cleveland, Ohio: Am. Inst. Min. Eng. Trans., vol. 56, p. 839, 1917.

[c] Orton, Edward, The Trenton limestone as a source of petroleum and natural gas in Ohio and Indiana: U. S. Geol. Survey Eighth Ann. Rept., p. 645, 1889.

[d] Personal communication.

[e] Stebinger, Eugene, Possibilities of oil and gas in north-central Montana: U. S. Geol. Survey Bull. 641, p. 73, 1916.

[f] Knapp, I. N., discussion of paper by R. W. Johnson, The rôle and fate of connate water in oil and gas sands: Am. Inst. Min. Eng. Trans., vol. 51, p. 593, 1915.

[g] Knapp, I. N., discussion of paper by W. H. Kobbe, The recovery of petroleum from unconsolidated sands: Idem, vol. 56, p. 825, 1917.

[h] McMurray, W. F., and Lewis, J. O., Underground wastes in oil and gas fields and methods of prevention: Bur. Mines Tech. Paper 130, p. 13, 1916.

Dr. I. C. White[1] reports gas pressures in West Virginia ranging from 600 pounds to the square inch in the Big Injun sand to as much as 1,800 pounds in a sand 4,090 feet deep. Rogers[2] reported gas pressures of 800 to 1,100 pounds to the square inch in the so-called Clinton sand near Cleveland, Ohio.

Table 5 shows that in several localities there is a rough proportion between initial gas pressure and depth, especially in the deeper sands. It is well recognized that gases forming from organic matter develop pressure when confined. To what extent these gas pressures or "rock pressures" are due to this or other causes is problematic, but whatever the source or origin of the gases and the causes of the pressure, the table suggests that there have been adjustments of pressure according to depth. It seems probable that hydrostatic pressure, weight of superincumbent strata, rock movements, deep-seated thermal conditions, the long-continued formation of natural gases, and the resistance to fluid movements through the strata all enter into the causes for "rock pressure." In other words, "rock pressures" are not necessarily "fossil pressures" but represent a summation of effects from remote time up to the present.

## CHARACTERISTICS OF THE APPALACHIAN OIL AND GAS FIELD WATERS.

### DEEP-SEATED BRINES AND THEIR COMPARISON WITH SEA WATER.

As the result of our studies we have concluded that the deep-seated Appalachian oil and gas field brines are, in part, the derivatives of former ocean water. Certain fundamental differences in composition, however, exist between ocean water and the waters under consideration. These differences have been noted in the literature[3] and are strikingly shown by Table 6. In the part of the table on page 30 analyses of the dissolved solids are expressed as percentages of the several constituents. The proportions of total dissolved solids in the different waters are also shown here, in terms of grams per kilogram or grams per liter. On page 31 are shown ratios of some of the constituents to chlorine. As the chlorine content of the dissolved solids in the waters under comparison is more uniform than that of the other constituents or of the total dissolved solids themselves, the ratios of the different constituents to chlorine are used as a basis for comparison. The ratios are first stated in terms of the actual percentages of the dissolved solids. In the lower part of the table these ratios are expressed in terms of the chemical reacting values of the constituents. The principle of reacting values has been applied in the interpretation and comparison of water analyses by several American investigators, among whom may be mentioned Stabler,[1] Palmer,[2] Spencer,[3] Emmons and Harrington,[4] Van Winkle,[5] Waring,[6] Clapp,[7] Siebenthal,[8] and Rogers.[9]

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[1] Personal communication.

[2] Rogers, G. S., The Cleveland gas field, Cuyahoga County, Ohio: U. S. Geol. Survey Bull. 661, p. 37, 1917.

[3] Hunt, T. S., Chemical and geological essays, pp. 11–12, Boston, 1875. Palmer, Chase, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, Table 2, opposite p. 14, 1911. Washburne, C. W., Chlorides in oil-field waters: Am. Inst. Min. Eng. Trans, vol. 48, pp. 687–693, 1914.

TABLE 6.—*Comparison between ocean water and Appalachian oil and gas field brines.*

| | Ocean water. | | Bitterns derived from concentration of ocean water. | | Appalachian oil and gas field waters. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | Pennsylvania. | | | Ohio. | |
| | | | | | 5 | 6 | 7 | 8 | 9 |
| $SiO_2$ | | | | | 0.01 | | | 0.06 | 0.41 |
| $(Al, Fe)_2O_3$ | | | | | .03 | | Trace. | | |
| $Fe''$ | | | | | .08 | 0.06 | 0.05 | .01 | [a].10 |
| Al | | | | | | | | .10 | .70 |
| Ca | 1.20 | 1.18 | 0.26 | | 8.57 | 9.56 | 8.40 | 8.19 | 5.18 |
| Sr | | | | | .16 | 1.31 | Trace. | | |
| Ba | | | | | None. | Trace. | Trace. | | |
| Mg | 3.71 | 3.59 | 3.72 | 10.05 | 1.46 | .94 | 1.47 | 1.30 | 1.63 |
| Na | 30.54 | 31.08 | 32.06 | 20.39 | 27.34 | 24.50 | 27.59 | 27.82 | 29.88 |
| K | 1.11 | .71 | .78 | 2.25 | .20 | 1.97 | .10 | .49 | .96 |
| $CO_3$ | .05 | .18 | | | None. | None. | None. | None. | None. |
| $HCO_3$ | .31 | | | | None. | | None. | .03 | .70 |
| $SO_4$ | 7.68 | 7.72 | 5.78 | 14.64 | .02 | .02 | .10 | None. | None. |
| Cl | 55.21 | 54.39 | 56.18 | 49.99 | 61.97 | 61.38 | 62.29 | 62.00 | 60.44 |
| Br, I | .19 | 1.15 | 1.22 | 2.68 | .16 | .26 | | | |
| | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| Total dissolved solids, grams per kilogram | 33.01–37.37 | 37.66 | 275.46 | 337.12 | 122.16 | 263.64 | 131.89 | [b]141.13 | [b]53.06 |

[a] Total iron. [b] Grams per liter.

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[1] Stabler, Herman, Industrial water analyses and their interpretation by the engineer: Eng. News, vol. 60, p. 355, 1908.

[2] Palmer, Chase, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, pp. 12–14, 1911; Mineralogy of waters from artesian wells at Charleston, S. C.: U. S. Geol. Survey Prof. Paper 90, pp. 92–93, 1914.

[3] Spencer, A. C., Chalcocite enrichment: Econ. Geology, vol. 8, p. 646, 1913.

[4] Emmons, W. H., and Harrington, G. L., A comparison of waters of mines and hot springs: Econ. Geology, vol. 8, p. 661, 1913.

[5] Van Winkle, Walton, Quality of the surface waters of Washington: U. S. Geol. Survey Water-Supply Paper 339, pp. 34–35, 1914; Quality of the surface waters of Oregon: U. S. Geol. Survey Water-Supply Paper 363, pp. 37–38, 1914.

[6] Waring, G. A., Springs of California: U. S. Geol. Survey Water-Supply Paper 338, pp. 22–23, 1914.

[7] Clapp, C. H., Sharp Point hot spring, Vancouver Island, British Columbia: Canada Geol. Survey Summary Rept. for 1913, pp. 80–83, 1914.

[8] Siebenthal, C. E., Origin of the zinc and lead deposits of the Joplin region, Missouri, Kansas, and Oklahoma: U. S. Geol. Survey Bull. 606, 1915.

[9] Rogers, G. S., The interpretation of water analyses by the geologist: Econ. Geology, vol. 12, pp. 56–88, 1917; Chemical relations of the oil-field waters in San Joaquin Valley, Cal.: U. S. Geol. Survey Bull. 653, 1917.

TABLE 6.—*Comparison between ocean water and Appalachian oil, etc.*—Contd.

**Ratios of the percentages of certain constituents to that of chlorine.**

| | Ocean water. | | Bitterns derived from concentration of ocean water. | | Appalachian oil and gas field waters. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Pennsylvania. | | | Ohio. | |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Na | 0.553 | 0.571 | 0.571 | 0.408 | 0.441 | 0.399 | 0.443 | 0.449 | 0.494 |
| Ca | .022 | .022 | .005 | .000 | .138 | .156 | .135 | .132 | .086 |
| Mg | .067 | .066 | .066 | .201 | .024 | .015 | .024 | .021 | .027 |
| $SO_4$ | .139 | .142 | .103 | .292 | .0003 | .0003 | .002 | .000 | .000 |

**Ratios of the reacting values [a] of certain constituents to that of chlorine.**

[Per thousand of chlorine.]

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Na | 852.5 | 880.2 | 880.2 | 628.9 | 679.8 | 615.1 | 682.9 | 692.1 | 761.5 |
| Ca | 38.4 | 38.4 | 8.19 | ........ | 244.9 | 275.7 | 238.7 | 233.8 | 151.7 |
| Mg | 196.6 | 192.5 | 193.0 | 586.2 | 68.8 | 44.7 | 68.8 | 61.1 | 78.6 |
| $SO_4$ | 102.7 | 104.9 | 76.0 | 216.1 | .2 | .2 | 1.19 | .0 | .0 |

[a] The meaning of the term "reacting value" is explained by Herman Stabler (Some stream waters of the western United States: U. S. Geol. Survey Water-Supply Paper 274, p. 167, 1911) as follows: "If the number of parts per million (or per thousand or per hundred) of each radicle found by analysis be multiplied by its reaction coefficient (reciprocal of combining weight), a number will be obtained which may be called the 'reacting value' for that analysis."

1. Mean of 77 analyses of ocean water from many localities, collected by the *Challenger* expedition, W. Dittmar, analyst. *Challenger* Rept., Physics and chemistry, vol. 1, p. 203, 1884. Total dissolved solids, 3.301 to 3.737 per cent. Analysis revised to show bicarbonates by R. C. Wells, U. S. Geol. Survey Professional Paper 120-A, p. 15, 1918.
2. Analysis of Mediterranean ocean water. Specific gravity of water, 1.0258. J. Usiglio, analyst. Annales chim. phys., 3d ser., vol. 27, pp. 92–172, 1849. Analysis reduced to ionic form and to percentages of total solids by F. W. Clarke, Data of geochemistry, 3d ed., U. S. Geol. Survey Bull. 616, p. 219, 1916.
3. Analysis of Mediterranean ocean water concentrated from density of 1.0258 to density of 1.21. Reference same as that for 2.
4. Analysis of Mediterranean ocean water concentrated from density of 1.0258 to density of 1.264. Reference same as that for 2.
5. Analysis of brine from Hundred-foot sand, probably of early Mississippian age; depth, 1,170 feet±. Sample collected from an old oil well, August 15, 1915, on McGrath farm, Center Township, Butler County, Pa. Specific gravity of water, 1.0876. R. C. Wells, analyst. The amount of sample available for analysis was insufficient for a direct determination of the total carbon dioxide, if present.
6. Analysis of brine from sandstone of early Devonian age, depth 6,260± to 6,300 feet. From gas well 8 miles southwest of Imperial, Washington County, Pa. Specific gravity of water, 1.211. George Steiger, analyst. Quoted by F. W. Clarke (Water analyses from the laboratory of the United States Geological Survey: U. S. Geol. Survey Water-Supply Paper 364, p. 9, 1914).
7. Analysis of brine from Hundred-foot sand, probably of early Mississippian age, depth 1,359 feet. Sample collected by G. B. Richardson from old oil well on farm of Charles Hoffman, 5 miles northeast of Butler, Pa. W. B. Hicks and R. K. Bailey, analysts. Quoted by G. B. Richardson (Note on the diffusion of sodium chloride in Appalachian oil-field waters: Washington Acad. Sci. Jour., vol. 7, pp. 73–75, 1917).
8. Analysis of brine from Big lime sand, of late Mississippian age, depth 1,431 to 1,444 feet. Sample collected by R. Van A. Mills, April 24, 1915, from an old oil well in an old oil and gas field, well No. 5 on F. Mellotte farm, in the northeast corner of Malaga Township, Monroe County, Ohio. S. C. Dinsmore, analyst.
9. Analysis of brine from Berea sand, of early Mississippian age, depth 1,748 to 1,760 feet. Sample collected by R. Van A. Mills, April 28, 1915, from a gas well 14 months old, on the Gulic farm. 1 mile west of Summerfield, Marion Township, Noble County, Ohio. S. C. Dinsmore, analyst.

It will be observed, by referring to Table 6 and to the analyses quoted on pages 33–39, that the concentration of the Appalachian oil and gas field brines ranges from slightly less to several times greater than that of ocean water. The ratios of sodium to chlorine, magnesium to chlorine, and sulphate to chlorine are all smaller in the oil and gas field waters than in ocean water, sulphate being comparatively absent in the oil and gas field waters. In contrast to this, the ratios of calcium to chlorine in the oil and gas field waters are much greater than in ocean water.

By comparing the analyses of bitterns derived from the evaporation of ocean water (3 and 4 in Table 6) with the analyses of oil and gas field waters shown in the same table, it will be observed that the differences ~~between~~ these types of brine become more striking as the evaporation of the ocean water progresses. This is due to the order of deposition ~~of the~~ dissolved constituents from ocean water during concentration. Calcium is deposited as carbonate and sulphate, but magnesium is retained longer in solution, the proportion of this constituent being consequently increased as calcium is eliminated. After the elimination of calcium, the proportion of sulphate remaining in solution increases, as is shown by analysis 4, Table 6. The sodium content of some bitterns derived from ocean water may be comparable with the sodium content of oil and gas field brines, but the other differences are none the less pronounced. These items make it apparent that the oil and gas field brines under consideration have not originated merely from the concentration of water such as now constitutes the ocean.

By applying Palmer's system of classification,[1] the reader will see (Table 7) that the properties of reaction of all the oil and gas field waters whose analyses are shown in Table 6 lie approximately between those of normal ocean water and the concentrated ocean water represented by analysis 4. The properties expressed under 9, Table 7, approach most nearly those of normal ocean water, and the properties expressed under 6, Table 7, approach most nearly those of the concentrated ocean water (4). Although, as expressed by Palmer's classification, the properties of reaction of the waters under comparison have striking similarities, it must be noted, as shown in the preceding discussion, that the saltness of normal and concentrated ocean waters is due partly to sulphate, whereas the saltness of oil and gas field waters is due almost entirely to chloride. It should also be noted that the proportion of magnesium in the constituents of normal and concentrated ocean water is greater and the proportion of calcium is less than in the constituents of the oil and gas field brines. Water with the properties expressed under 9, Table 7, and the composition expressed under 9, Table 6, might be derived from normal ocean water by concentration if practically all the sulphate and part of the magnesium and sodium were removed and a certain amount of calcium added. In the succeeding pages we show some of the probabilities regarding these changes.

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[1] Palmer, Chase, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, 1911.

TABLE 7.—*Properties of reaction of ocean water and of Appalachian oil and gas field waters, expressed in percentages.*[a]

| Properties of reaction. | Ocean water. | | Bitterns derived from the concentration of ocean water. | | Appalachian oil and gas field waters. | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Pennsylvania. | | | Ohio. | |
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Primary salinity | 78.8 | 79.4 | 81.6 | 53.2 | 69.2 | 66.5 | 69.0 | 70.4 | 77.2 |
| Secondary salinity | 20.8 | 20.2 | 18.4 | 46.8 | 30.8 | 33.5 | 31.0 | 29.6 | 22.2 |
| Secondary alkalinity | .4 | .4 | .0 | .0 | .0 | .0 | .0 | .0 | .6 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

[a] The waters whose properties of reaction are shown in this table are the same as those shown in Table 6.

## ANALYSES OF APPALACHIAN OIL AND GAS FIELD WATERS.

TABLE 8.—*Analyses of waters from the Hundred-foot sand.*

**Grams per liter.**

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | ........ | 0.24 | 0.18 | 0.15 | 0.11 | 0.78 | 0.01 |
| Fe | 0.07 | .01 | 0.04 | .02 | ........ | .02 | [a].11 |
| Al | ........ | .49 | .26 | .12 | [b].12 | .57 | [b].04 |
| Ca | 12.21 | 10.29 | 10.85 | 7.25 | 7.48 | 13.59 | 11.40 |
| Sr | ........ | ........ | ........ | ........ | ........ | ........ | [c].21 |
| Mg | 2.14 | 1.85 | 1.71 | 1.35 | 1.35 | 1.46 | 1.95 |
| Na | 40.10 | 33.76 | 31.46 | 27.59 | 27.37 | 41.74 | 36.30 |
| K | .14 | .26 | 2.67 | .16 | Present. | 2.13 | .26 |
| $HCO_3$ | None. | .02 | .03 | .03 | .02 | .07 | None. |
| $SO_4$ | .14 | .12 | .22 | None. | None. | None. | Trace. |
| Cl | 90.54 | 78.78 | 77.39 | 59.61 | 58.52 | 96.56 | 82.35 |
| Br | ........ | ........ | ........ | ........ | ........ | ........ | .22 |
| | 145.34 | 125.82 | 124.81 | 96.28 | 94.97 | 156.92 | 132.85 |
| Specific gravity | [d]1.102 | ........ | ........ | ........ | ........ | ........ | 1.088 |

**Reacting values, in milligram equivalents per liter.**[e]

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Fe | 2.5 | 0.5 | 1.2 | ........ | ........ | 1.0 | 0.4 |
| Ca | 610.5 | 513.7 | 541.7 | 362.0 | 374.0 | 679.0 | 569.1 |
| Mg | 176.1 | 152.3 | 140.7 | 111.0 | 111.0 | 120.0 | 160.4 |
| Na | 1,743.4 | 1,468.0 | 1,368.0 | 1,200.0 | 1,190.0 | 1,815.0 | 1,578.0 |
| K | 3.6 | 6.0 | 68.0 | 4.1 | ........ | 54.0 | 6.7 |
| Sr | ........ | ........ | ........ | ........ | ........ | ........ | 4.9 |
| Total basic radicles | 2,536.1 | 2,140.5 | 2,119.6 | 1,677.1 | 1,675.0 | 2,669.0 | 2,319.5 |
| $HCO_3$ | ........ | .4 | .5 | ........ | ........ | 1.0 | None. |
| $SO_4$ | 2.9 | 2.6 | 4.5 | ........ | ........ | None. | Trace. |
| Cl | 2,553.4 | 2,222.0 | 2,182.0 | 1,681.0 | 1,650.0 | 2,723.0 | 2,322.0 |
| Br | ........ | ........ | ........ | ........ | ........ | ........ | 3.0 |
| Total acid radicles | 2,556.3 | 2,225.0 | 2,187.0 | 1,681.0 | 1,650.0 | 2,724.0 | 2,325.0 |

[a] Ferrous iron.
[b] $Al_2O_3+Fe_2O_3$.
[c] Barium absent.
[d] Calculated from content of salts.
[e] It is believed that these terms will be clear without elaborate explanation. A solution containing a milligram equivalent per liter would be "thousandth normal" in the terms of analytical chemistry, a milligram equivalent of any element or radicle being as many milligrams of the element or radicle as are equivalent in capacity for chemical reaction to 1.008 milligrams of hydrogen or 8.000 milligrams of oxygen.

TABLE 8.—*Analyses of waters from the Hundred-foot sand*—Continued.

**Reacting values, in per cent.**

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| Sr | | | | | | | 0.1 |
| Ca | 12.0 | 11.6 | 12.4 | 10.8 | 11.3 | 12.4 | 12.2 |
| Mg | 3.4 | 3.4 | 3.2 | 3.3 | 3.4 | 2.2 | 3.5 |
| Na | 34.5 | 34.9 | 32.8 | 35.8 | 35.3 | 34.4 | 34.1 |
| K | .1 | .1 | 1.6 | .1 | | 1.0 | .1 |
| $SO_4$ | .1 | | .1 | | | | |
| Cl | 49.9 | 50.0 | 49.9 | 50.0 | 50.0 | 50.0 | 49.9 |
| Br | | | | | | | .1 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

**Approximate percentages of principal salts.**

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|
| $CaCl_2$ | 23.2 | 22.5 | 23.9 | 21.0 | 22.6 | 25.0 | 24.1 |
| $MgCl_2$ | 5.8 | 5.7 | 5.3 | 5.5 | 5.6 | 3.8 | 5.7 |
| NaCl | 70.8 | 71.5 | 66.7 | 73.2 | 71.8 | 68.6 | 69.9 |
| KCl | .2 | .3 | 4.1 | .3 | | 2.6 | .3 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

1. Brine from Hundred-foot sand; depth 1,359 feet; well No. 2, Charles Hoffman farm, Oakland Township, Butler County, Pa. Sample collected in October, 1915. Na and K determined by W. B. Hicks; the rest of the determinations by R. K. Bailey, Econ. Geology, vol. 12, p. 39, 1917.

2. Brine from Hundred-foot sand; depth 1,018 to 1,035 feet; well No. 1, Harlan Book farm, Muddy Creek, Clay Township, Butler County, Pa. This is a new oil well which had just been completed when the sample was collected in October, 1915. Well drilled by Parker & Edwards Co. S. C. Dinsmore, analyst.

3. Brine from Hundred-foot sand; well No. 2, Mary B. Heist farm, Center and Butler townships, Butler County, Pa. Sample collected in September, 1915. S. C. Dinsmore, analyst.

4. Brine from Hundred-foot sand; depth 1,361 to 1,387 feet; well No. 3, W. H. Cooper farm, Penn Township, Butler County, Pa. This was an oil well drilled about one year prior to the collecting of the sample. S. C. Dinsmore, analyst.

5. Same water as No. 4. Chase Palmer, analyst.

6. Brine from Hundred-foot sand, well on the Charles Kaiser farm, eastern part of Summit Township, Butler County, Pa. Sample collected in September, 1915. S. C. Dinsmore, analyst.

7. Brine from Hundred-foot sand; depth 1,170± feet; old McCarrier & Wald well on McGrath farm, Pine tract, Center Township, Butler County, Pa. Sample collected in August, 1915. Sample was clear when collected, but reddish-yellow precipitate formed on standing 24 hours. R. C. Wells, analyst.

TABLE 9.—*Analyses of waters from various sands.*

**Grams per liter.**

| | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | | 0.019 | 1.87 | 0.080 | 0.05 | 0.09 | 0.02 | 0.08 |
| Fe | Present. | .007 | .02 | Trace. | [a] None. | .02 | [a] .08 | .01 |
| Al | Present. | | | .011 | [b] .05 | .15 | None. | .56 |
| Ca | 0.89 | .060 | 7.58 | .050 | 2.89 | 11.56 | 5.58 | 11.36 |
| Sr | | | | | [c] .07 | | .04 | |
| Mg | .32 | .030 | 1.62 | .010 | .80 | 1.83 | 1.03 | 1.63 |
| Na | 9.81 | 2.640 | 30.45 | .299 | 19.50 | 39.27 | 23.85 | 38.32 |
| K | | | | .055 | .23 | .70 | .25 | .51 |
| $HCO_3$ | .16 | .102 | .09 | .261 | .26 | .03 | .32 | .03 |
| $SO_4$ | | None. | None. | None. | None. | None. | None. | None. |
| Cl | 17.28 | 4.200 | 64.93 | .435 | 38.54 | 87.50 | 50.33 | 84.71 |
| Br | | | | | .16 | | .15 | |
| Total | 28.46 | 7.123 | 106.56 | 1.201 | 62.55 | 141.15 | 81.65 | 137.21 |
| Specific gravity | | | | | 1.044 | [d] 1.102 | 1.056 | |

[a] Ferrous iron. [b] $Al_2O_3+Fe_2O_3$. [c] Barium absent. [d] Calculated from salt content.

TABLE 9.—*Analyses of waters from various sands*—Continued.

**Reacting values, in milligram equivalents per liter.**

| | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|
| Fe | | | 1.0 | | None. | 0.6 | 3.0 | 0.5 |
| Ca | 22.3 | 3.0 | 378.0 | 2.5 | 144.3 | 577.9 | 278.6 | 567.8 |
| Mg | 25.9 | 2.5 | 133.0 | .8 | 65.8 | 150.6 | 84.8 | 134.0 |
| Na | 426.4 | 114.8 | 1,324.0 | 13.0 | 847.8 | 1,707.0 | 1,037.0 | 1,666.0 |
| K | | | | 1.4 | 5.9 | 17.8 | 6.4 | 13.0 |
| Sr | | | | | 1.6 | | .9 | |
| Total basic radicles | 474.6 | 120.3 | 1,836.0 | 17.7 | 1,067.4 | 2,453.9 | 1,410.7 | 2,381.3 |
| $HCO_3$ | [a] 2.5 | | | 4.3 | 4.3 | 1.0 | 5.3 | 1.0 |
| $SO_4$ | | | | None. | None. | None. | None. | None. |
| Cl | 487.3 | 118.5 | 1,831.0 | 12.3 | 1,087.0 | 2,468.0 | 1,419.0 | 2,389.0 |
| Br | | | | | 2.0 | | 1.9 | |
| Total acid radicles | 489.8 | 118.5 | 1,831.0 | 16.6 | 1,093.3 | 2,469.0 | 1,426.2 | 2,390.0 |

**Reacting values, in per cent.**

| | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|
| Fe | | | | | | | 0.1 | |
| Ca | 2.3 | 1.2 | 10.3 | 7.5 | 6.6 | 11.8 | 9.8 | 11.9 |
| Mg | 2.6 | 1.1 | 3.6 | 2.4 | 3.1 | 3.0 | 3.0 | 2.8 |
| Na | 45.1 | 47.7 | 36.1 | 35.9 | 40.0 | 34.8 | 36.9 | 35.0 |
| K | | | | 4.2 | .3 | .4 | .2 | .3 |
| $HCO_3$ | .2 | | | 12.9 | .2 | | .2 | |
| Cl | 49.8 | 50.0 | 50.0 | 37.1 | 49.7 | 50.0 | 49.8 | 50.0 |
| Br | | | | | .1 | | | |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

**Approximate percentages of principal salts.**

| | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|
| $CaCl_2$ | 4.4 | 2.4 | 12.3 | 14.5 | 12.7 | 22.7 | 18.9 | 23.0 |
| $MgCl_2$ | 4.3 | 1.8 | 6.6 | 4.0 | 5.0 | 5.1 | 4.9 | 4.7 |
| NaCl, KCl | 91.3 | 95.8 | 81.1 | | | | | |
| NaCl | | | | 69.9 | 81.6 | 71.3 | 75.6 | 71.6 |
| KCl | | | | 11.6 | .7 | .9 | .6 | .7 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

[a] Includes HS.

8. Brine from Five Hundred-foot sand; depth 420 feet; well No. 7, Vorhies farm, Center Township, Noble County, Ohio. Sample collected in December, 1915. The well from which the sample was collected is one of a group of several shallow-sand wells that yielded small amounts of oil for a few years. In March, 1917, the well was not being pumped. The sample was clear when collected, but a rusty yellow precipitate formed during the first 24 hours after the water was collected. On standing a few weeks this yellowish precipitate was replaced by a black precipitate of ferrous sulphide. It is not known whether the iron was originally present or was contributed by the iron piping in the well, but it is evident that a soluble sulphide was present and that it reacted with the iron upon standing. Chase Palmer, analyst.

9. Brine from Cow Run sand; depth 900 feet; well of American Oil Development Co. on Cave Run, Pleasants County, W. Va. Production of water 2 barrels daily. S. C. Dinsmore, analyst. Reeves. Frank, Econ. Geology, vol. 12, p. 374, 1917.

10. Brine from Salt sand; depth 1,600 feet; S. E. Elliot well No. 12, South Penn Oil Co., Bell Run, Lafayette district, Wirt County, W. Va. Production of water 25 barrels daily. S. C. Dinsmore, analyst. Reeves, Frank, op. cit., p. 374.

11. Artesian water from shallow-sand well on Neigh farm, Summit Township, Butler County, Pa. Water comes from depth of about 350 feet. S. C. Dinsmore, analyst.

12. Brine from Maxton sand; depth 905 feet; well No. 1, David Bintz farm, sec. 33, Malaga Township, Monroe County, Ohio, near Monroefield. Well drilled in August, 1912; sample collected in November, 1916. Very dark green to black oil, containing brownish-yellow specks collected with the water. Rust-colored precipitate at bottom of bottle after standing 48 hours. R. C. Wells, analyst.

13. Brine from Big lime sand; depth 1,431 to 1,444 feet; well No. 5, F. Mellotte farm, northeast corner of Malaga Township, Monroe County, Ohio. Sample collected April 24, 1915. S. C. Dinsmore, analyst.

14. Brine from Big lime sand; depth 1,339 to 1,349 feet; well No. 1, Egger Bros.' farm, sec. 10, Malaga Township, Monroe County, Ohio, near Miltonsburg. Well completed in January, 1916; sample collected in September, 1916. Gas well, initial open-flow production 1,500,000 cubic feet a day; initial gas pressure 360 pounds to the square inch. Production of water 1½ barrels a week. Black deposit on inside of bottle in air space just above water, also dirty-gray flocculent precipitate floating at top of water and a somewhat lighter-colored gray flocculent precipitate at bottom of bottle. No oil was present. R. C. Wells, analyst.

15. Brine from Keener sand; depth 1,451 to 1,469 feet; well No. 2, J. R. Scott farm, near Jerusalem, Sunsbury Township, Monroe County, Ohio. Sample collected April 24, 1915. S. C. Dinsmore, analyst.

TABLE 10.—*Analyses of waters from the Keener sand.*

Grams per liter.

| | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 0.08 | 0.14 | | 0.05 | 0.06 | 0.04 | 0.02 |
| Fe | .01 | .02 | | [a] .01 | | | .04 |
| Al | .35 | .62 | | [b] .05 | [b] .08 | | |
| Ca | 5.68 | 12.98 | 8.02 | 2.98 | 11.20 | 8.34 | 10.84 |
| Sr | | | | [c] .08 | | | |
| Mg | 1.04 | 1.69 | 1.42 | .82 | 1.82 | 1.48 | 2.99 |
| Na | 22.84 | 43.40 | 28.76 | 19.85 | 38.64 | 29.74 | 41.53 |
| K | .60 | 2.47 | | .23 | | | |
| $HCO_3$ | .08 | .04 | .03 | .17 | .04 | .03 | .03 |
| $SO_4$ | None. | None. | | None. | | None. | .01 |
| Cl | 48.46 | 97.96 | 62.48 | 38.89 | 83.88 | 64.10 | 91.70 |
| Br | | | | .11 | | | |
| | 79.15 | 159.32 | 100.71 | 63.24 | 135.72 | 103.73 | 147.16 |
| Specific gravity | | | | 1.043 | | | |

Reacting values, in milligram equivalents per liter.

| | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|---|---|---|---|---|---|---|---|
| Fe | 0.4 | 0.6 | | Trace. | | | 1.0 |
| Ca | 283.9 | 648.0 | 400.3 | 148.8 | 559.2 | 416.0 | 541.0 |
| Mg | 85.5 | 139.5 | 116.9 | 67.5 | 149.7 | 122.0 | 246.0 |
| Na | 993.0 | 1,887.0 | 1,250.0 | 863.1 | 1,680.0 | 1,293.0 | 1,806.0 |
| K | 15.0 | 63.0 | | 5.9 | | | |
| Sr | | | | 1.9 | | | |
| Total basic radicles | 1,377.8 | 2,738.1 | 1,767.2 | 1,087.2 | 2,388.9 | 1,831.0 | 2,594.0 |
| HCO | 1.0 | .6 | .6 | 2.8 | .7 | Trace. | |
| $SO_4$ | None. | None. | | None. | | None. | |
| Cl | 1,367.0 | 2,763.0 | 1,762.0 | 1,097.0 | 2,366.0 | 1,808.0 | 2,586.0 |
| Br | | | | 1.4 | | | |
| Total acid radicles | 1,368.0 | 2,763.6 | 1,762.6 | 1,101.2 | 2,366.7 | 1,808.0 | 2,586.0 |

Reacting values, in per cent.

| | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|---|---|---|---|---|---|---|---|
| Sr | | | | 0.1 | | | |
| Ca | 10.4 | 11.7 | 11.3 | 6.7 | 11.8 | 11.5 | 10.5 |
| Mg | 3.1 | 2.5 | 3.3 | 3.1 | 3.2 | 3.4 | 4.7 |
| Na | 36.0 | 34.7 | 35.4 | 39.8 | 35.0 | 35.1 | 34.8 |
| K | .5 | 1.1 | | .3 | | | |
| $HCO_3$ | | | | .1 | | | |
| Cl | 50.0 | 50.0 | 50.0 | 49.9 | 50.0 | 50.0 | 50.0 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

Approximate percentages of principal salts.

| | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
|---|---|---|---|---|---|---|---|
| $CaCl_2$ | 20.2 | 22.6 | 22.0 | 13.2 | 23.0 | 22.5 | 20.5 |
| $MgCl_2$ | 5.2 | 4.1 | 5.6 | 5.1 | 5.3 | 5.6 | 8.0 |
| NaCl | 73.2 | 70.3 | 72.4 | 81.0 | 71.7 | 71.9 | 71.5 |
| KCl | 1.4 | 3.0 | | .7 | | | |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

[a] Ferrous iron. [b] $Al_2O_3+Fe_2O_3$. [c] Barium absent.

16. Brine from Keener sand; depth 1,465 to 1,471 feet; well No. 1, Schroeder heirs' farm, 1¼ miles south of Miltonsburg, Malaga Township, Monroe County, Ohio. Rate of production from this new well, 150 barrels of oil a day, with large amounts of gas and small amounts of brine when the sample was collected, April 24, 1915. The well was the first in the field and was drilled in March, 1915. S. C. Dinsmore, analyst.

17. Brine from Keener sand; depth 870 to 880 feet; well No. 2, Mancel Secrest farm, 1¼ miles southeast of Chaseville, Seneca Township, Noble County, Ohio. Sample collected May 1, 1915. S. C. Dinsmore, analyst.

18. Brine from Keener sand; well No. 1 (gas well), A. Clause farm, NE. ¼ sec. 10, Malaga Township, Monroe County, Ohio, near Miltonsburg. Well completed February 18, 1916; sample collected in September, 1916. Chase Palmer, analyst.

19. Brine from Keener sand; depth 1,302 feet; well No. 4 (oil well), C. J. Clause farm, sec. 27, Malaga Township, Monroe County, Ohio, near Monroefield. Well drilled in July, 1913; sample collected November 7, 1916. Dull amber-colored oil was collected with the water. The water was clear when collected, but a reddish rusty precipitate settled at the bottom of the bottle within 24 hours. R. C. Wells, analyst.

20. Brine from Keener sand; depth 1,451 to 1,469 feet; well No. 2, J. R. Scott farm, NE. ¼ sec. 23, Sunsbury Township, Monroe County, Ohio, half a mile southeast from Jerusalem village. Old oil and gas well, drilled in 1904. The well is reported to have flowed and sprayed oil at the rate of 350 barrels a day with very little water at first. In June, 1916, it was yielding daily 2 barrels of oil together with 5 barrels of water. Sample collected in August, 1916. Chase Palmer, analyst.

21. Brine from the same well as that described under No. 16 but collected in September, 1916. Chase Palmer, analyst.

22. Brine from Keener sand; depth 1,700 feet; American Oil Co.'s well on J. T. Craw farm, Cave Run, Pleasants County W. Va. S. C. Dinsmore, analyst. Reeves, Frank, Econ. Geology, vol. 12, p. 374, 1917.

**Table 11.**—*Analyses of waters from the Big Injun sand.*

**Grams per liter.**

| | 23 | 24 | 25 | 26 |
|---|---|---|---|---|
| $SiO_2$ | 0.70 | 0.21 | 0.19 | 0.13 |
| Fe | .02 | .03 | .02 | .04 |
| Al | .60 | ........ | ........ | ........ |
| Ca | 12.22 | 11.94 | 10.24 | 17.12 |
| Mg | 2.89 | 1.81 | 1.63 | 2.96 |
| Na | 45.88 | 37.67 | 33.47 | 53.69 |
| K | .35 | | | |
| $HCO_3$ | .02 | .04 | .01 | ........ |
| $SO_4$ | None. | None. | None. | None. |
| Cl | 102.14 | 84.35 | 74.38 | 121.63 |
| | 164.82 | 136.05 | 119.94 | 195.63 |

**Reacting values, in milligram equivalents per liter.**

| | 23 | 24 | 25 | 26 |
|---|---|---|---|---|
| Fe | 0.6 | 1.0 | 1.0 | 1.0 |
| Ca | 610.1 | 596.0 | 511.0 | 855.0 |
| Mg | 236.6 | 149.0 | 134.0 | 244.0 |
| Na | 1,995.0 | 1,710.0 | 1,455.0 | 2,334.0 |
| K | 9.0 | ........ | ........ | ........ |
| Total basic radicles | 2,851.3 | 2,456.0 | 2,101.0 | 3,434.0 |
| $HCO_3$ | .3 | ........ | ........ | ........ |
| $SO_4$ | None. | None. | None. | None. |
| Cl | 2,181.0 | 2,379.0 | 2,097.0 | 3,430.0 |
| Total acid radicles | 2,881.3 | 2,379.0 | 2,097.0 | 3,430.0 |

**Reacting values, in per cent.**

| | 23 | 24 | 25 | 26 |
|---|---|---|---|---|
| Ca | 10.6 | 12.5 | 12.2 | 12.4 |
| Mg | 4.1 | 3.1 | 3.2 | 3.6 |
| Na | 35.1 | 34.4 | 34.6 | 34.0 |
| K | .2 | ........ | ........ | ........ |
| Cl | 50.0 | 50.0 | 50.0 | 50.0 |
| | 100.0 | 100.0 | 100.0 | 100.0 |

**Approximate percentages of principal salts.**

| | 23 | 24 | 25 | 26 |
|---|---|---|---|---|
| $CaCl_2$ | 20.8 | 24.4 | 23.7 | 24.6 |
| $MgCl_2$ | 6.9 | 5.2 | 5.3 | 5.9 |
| NaCl | 71.9 | 70.4 | 71.0 | 69.5 |
| KCl | .4 | ........ | ........ | ........ |
| | 100.0 | 100.0 | 100.0 | 100.0 |

23. Brine from Big Injun sand; depth 1,200 feet; well No. 1, Henry H. Moore farm, near Summerfield, Marion Township, Noble County, Ohio. Sample collected April 27, 1915. S. C. Dinsmore, analyst.

24. Brine from Big Injun sand; depth 1,425 feet; Carter Oil Co.'s well No. 2, on Russell heirs' farm, near Paden City, Wetzel County, W. Va. Production of water 5 barrels daily. S. C. Dinsmore, analyst. Reeves, Frank, Econ. Geology, vol. 12, p. 374, 1917.

25. Brine from Big Injun sand; depth 1,355 feet; E. A. Bradley well No. 2, Fiel farm, Jackson Township, Monroe County, Ohio. Production of water 3 barrels daily. S. C. Dinsmore, analyst. Reeves, Frank, op. cit., p. 374.

26. Brine from Big Injun sand; depth 2,000 feet; South Penn Oil Co.'s well No. 1, Isaiah Baker farm, Muddy Creek, Tyler County, W. Va. Production of water 20 barrels daily. S. C. Dinsmore, analyst. Reeves, Frank, op. cit., p. 374.

TABLE 12.—*Analyses of waters from the Berea sand.*

**Grams per liter.**

| | 27 | 28 | 29 | 30 | 31 |
|---|---|---|---|---|---|
| $SiO_2$ | 0.090 | 0.22 | 0.14 | 0.08 | ........ |
| Fe | .006 | .06 | .01 | ........ | ........ |
| Al | .022 | .37 | .50 | ........ | ........ |
| Ca | .220 | 2.75 | 2.79 | 9.24 | 7.34 |
| Mg | .070 | .86 | 1.01 | 2.06 | 1.16 |
| Na | .475 | 15.85 | 19.49 | 32.66 | 25.82 |
| K | .055 | .51 | .50 | ........ | ........ |
| $HCO_3$ | .146 | .37 | .05 | .02 | .06 |
| $SO_4$ | None. | None. | None. | None. | None. |
| Cl | 1.045 | 32.07 | 38.69 | 72.60 | 55.46 |
| | 2.129 | 53.06 | 63.18 | 116.66 | 98.84 |
| Specific gravity | ........ | ........ | ........ | 1.08 | 1.06 |

**Reacting values, in milligram equivalents per liter.**

| | 27 | 28 | 29 | 30 | 31 |
|---|---|---|---|---|---|
| Fe | 0.2 | 2.0 | 0.3 | ........ | ........ |
| Ca | 11.0 | 137.3 | 139.3 | 461.3 | 366.5 |
| Mg | 5.7 | 71.0 | 83.0 | 169.6 | 95.5 |
| Na | 21.3 | 689.1 | 847.4 | 1,420.0 | 1,123.0 |
| K | 1.4 | 13.0 | 13.0 | ........ | ........ |
| Total basic radicles | 39.6 | 912.4 | 1,083.0 | 2,050.9 | 1,585.0 |
| $HCO_3$ | 2.4 | 6.1 | .8 | .4 | .9 |
| $SO_4$ | None. | None. | None. | None. | None. |
| Cl | 29.5 | 904.4 | 1,091.0 | 2,047.0 | 1,564.0 |
| Total acid radicles | 31.9 | 910.5 | 1,091.8 | 2,047.4 | 1,564.9 |

**Reacting values, in per cent.**

| | 27 | 28 | 29 | 30 | 31 |
|---|---|---|---|---|---|
| Fe | 0.3 | 0.1 | ........ | ........ | ........ |
| Ca | 17.3 | 7.5 | 6.4 | 11.3 | 11.7 |
| Mg | 8.9 | 3.9 | 3.8 | 4.1 | 3.1 |
| Na | 21.3 | 37.8 | 39.2 | 34.6 | 35.2 |
| K | 2.2 | .7 | .6 | ........ | ........ |
| $HCO_3$ | 3.8 | .3 | ........ | ........ | ........ |
| Cl | 46.2 | 49.7 | 50.0 | 50.0 | 50.0 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

**Approximate percentages of principal salts.**

| | 27 | 28 | 29 | 30 | 31 |
|---|---|---|---|---|---|
| $CaCl_2$ | 34.8 | 14.6 | 12.3 | 21.8 | 23.1 |
| $MgCl_2$ | 15.5 | 6.5 | 6.3 | 6.9 | 5.1 |
| NaCl | 43.4 | 77.1 | 79.9 | 71.3 | 71.8 |
| KCl | 6.3 | 1.8 | 1.5 | | |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

27. Brine from Berea sand; depth 2,141 to 2,162 feet; well No. 4 (old oil well), Taylor heirs' farm, 2 miles east of Woodsfield, Center Township, Monroe County, Ohio. Sample collected April 26, 1915, from a separating tank at the well; had probably undergone dilution after being brought to the surface. S. C. Dinsmore, analyst.

28. Brine from Berea sand; depth 1,748 to 1,760 feet; well No. 2 (gas well), Gulic farm, 1 mile west of Summerfield, Marion Township, Noble County, Ohio. Sample collected April 28, 1915. S. C. Dinsmore, analyst.

29. Brine from Berea sand; depth 1,570 to 1,592 feet; well No. 2, S. L. Murphy farm, near Chaseville, Seneca Township, Noble County, Ohio. Sample collected April 30, 1915. S. C. Dinsmore, analyst.

30. Brine from Berea sand; depth 1,727 to 1,740 feet; well No. 1 (old oil well), J. A. Adams farm, half a mile west of Barnesville, Warren Township, Belmont County, Ohio. The well was yielding 48 barrels of oil and 8 barrels of salt water a month when visited in June, 1916; the initial yield of oil from the well about 20 years prior to this was about 180 barrels of oil a month. Both oil and gas were produced in this field Sample collected July 24, 1916. Chase Palmer, analyst.

31. Brine from Berea sand; depth 2,141 to 2,162 feet; well No. 4 (old oil well), Taylor heirs' farm, 2 miles east of Woodsfield, Center Township, Monroe County, Ohio. The well had been yielding oil and salt water since 1905. Sample collected July 25, 1916; sample 27, collected from same well a year previously. Chase Palmer, analyst.

TABLE 13.—*Analyses of waters from various sands*

**Grams per liter.**

| | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 0.01 | Trace. | 0.05 | 0.12 | 0.05 | 0.03 | ........ | ........ |
| Fe | .07 | [a] 0.14 | .04 | .05 | ........ | .09 | 0.19 | ........ |
| Al | ........ | [b] .02 | ........ | .83 | [b] .08 | ........ | ........ | ........ |
| Ca | 10.16 | 13.79 | 7.91 | 15.82 | 15.36 | 10.28 | 30.50 | 2.58 |
| Sr | ........ | [c] .11 | ........ | ........ | ........ | ........ | [d] 4.30 | 1.05 |
| Mg | 1.48 | 2.22 | 1.47 | 1.87 | 2.04 | 1.54 | 3.00 | .44 |
| Na | 31.65 | 37.93 | 28.60 | 40.80 | 40.58 | 32.84 | 78.20 | 5.01 |
| K | ........ | .73 | .35 | .95 | .76 | ........ | 6.25 | .49 |
| $HCO_3$ | .05 | .04 | .03 | .03 | .02 | .03 | ........ | [e] .41 |
| $SO_4$ | .37 | .18 | .01 | .13 | Trace. | .04 | .06 | None. |
| Cl | 70.70 | 88.82 | 62.65 | 97.61 | 95.80 | 73.15 | 196.00 | 13.80 |
| Br | ........ | .19 | ........ | ........ | ........ | ........ | .85 | 1.11 |
| | 114.49 | 144.17 | 101.18 | 158.21 | 154.69 | 118.00 | 319.35 | 24.89 |
| Specific gravity | ........ | 1.099 | ........ | ........ | ........ | ........ | 1.211 | 1.160 |
| **Reacting values, in milligram equivalents per liter.** | | | | | | | | |
| Fe | 2.0 | 0.5 | 1.0 | ........ | ........ | 3.0 | 7.0 | ........ |
| Ca | 507.0 | 688.3 | 395.0 | 790.5 | 766.8 | 513.0 | 1,523.0 | 129.0 |
| Mg | 122.0 | 182.8 | 121.0 | 154.0 | 167.9 | 127.0 | 247.0 | 35.6 |
| Na | 1,376.0 | 1,649.0 | 1,243.0 | 1,774.0 | 1,764.0 | 1,428.0 | 3,400.0 | 217.8 |
| K | ........ | 18.7 | 9.0 | 24.4 | 19.5 | ........ | 160.0 | 12.5 |
| Sr | ........ | 2.5 | ........ | ........ | ........ | ........ | 98.0 | 24.0 |
| Total basic radicles | 2,007.0 | 2,541.8 | 1,769.0 | 2,742.9 | 2,718.2 | 2,071.0 | 5,435.0 | 418.9 |
| $HCO_3$ | ........ | .7 | ........ | ........ | ........ | ........ | ........ | Trace. |
| $SO_4$ | ........ | 3.7 | ........ | 2.3 | Trace. | ........ | 1.0 | None. |
| Cl | 1,998.0 | 2,505.0 | 1,767.0 | 2,752.0 | 2,702.0 | 2,063.0 | 5,527.0 | 389.2 |
| Br | ........ | 2.4 | ........ | ........ | ........ | ........ | 10.0 | 13.9 |
| Total acid radicles | 1,998.0 | 2,511.8 | 1,767.0 | 2,754.3 | 2,702.0 | 2,063.0 | 5,538.0 | 403.1 |
| **Reacting values, in per cent.** | | | | | | | | |
| Sr | ........ | ........ | ........ | ........ | ........ | ........ | 0.9 | 3.0 |
| Ca | 12.7 | 13.8 | 11.2 | 14.4 | 14.2 | 12.5 | 13.8 | 16.0 |
| Mg | 3.0 | 3.6 | 3.4 | 2.8 | 3.1 | 3.1 | 2.2 | 4.4 |
| Na | 34.3 | 32.2 | 35.2 | 32.4 | 32.3 | 34.4 | 31.6 | 25.1 |
| K | ........ | .4 | .2 | .4 | .4 | ........ | 1.5 | 1.5 |
| Cl | 50.0 | 50.0 | 50.0 | 50.0 | 50.0 | 50.0 | 49.9 | 48.3 |
| Br | ........ | ........ | ........ | ........ | ........ | ........ | .1 | 1.7 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |
| **Approximate percentages of principal salts.** | | | | | | | | |
| $CaCl_2$ | 24.7 | 26.6 | 21.8 | 27.8 | 27.6 | 24.3 | 28.4 | 32.3 |
| $MgCl_2$ | 5.1 | 6.1 | 5.7 | 4.6 | 5.2 | 5.2 | 3.7 | 7.7 |
| NaCl | 70.2 | 66.3 | 71.8 | 66.4 | 66.2 | 70.5 | 64.2 | 55.8 |
| KCl | | 1.0 | .7 | 1.2 | 1.0 | | 3.7 | 4.2 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

[a] Ferrous iron. [b] $Al_2O_3+Fe_2O_3$. [c] Barium absent. [d] Trace of Ba. [e] Trace of $CO_2$.

32. Brine from Second sand; depth 948 to 964 feet; well No. 19, A. B. Kelly farm, Tionesta Township, Forest County, Pa. Production of water was originally 5 barrels daily but had declined to 3 barrels daily when the sample was collected. S. C. Dinsmore, analyst. Reeves, Frank, Econ. Geology, vol. 12, p. 374, 1917.

33. Brine from Third or Fourth (?) sand; depth 1,842 to 1,870 feet; well No. 2 (oil well), Cyrus Step farm, Penn Township, Butler County, Pa. The initial production of oil from this well, about 20 years ago, is reported to have been 100 barrels of oil daily, with very little water. In August, 1915, when the sample was collected, the well was yielding three-fourths of a barrel of oil and 10 barrels of salt water a day. The usual yellowish precipitate formed at the bottom of the bottle upon standing. R. C. Wells, analyst.

34. Brine from Fourth sand; depth 1,623 to 1,654 feet; South Penn Oil Co's. well No. 1 on D. C. Rankin farm, Fairview Township, Butler County, Pa. Production of water 1½ barrels daily. S. C. Dinsmore, analyst. Reeves, Frank, op. cit., p. 374.

35. Brine from Bowlder sand, depth 1,701 to 1,720± feet; well No. 1 (new oil well), Mrs. Henry Welsh farm, Penn Township, Butler County, Pa. Sample collected in September, 1915. S. C. Dinsmore, analyst.

36. Duplicate of sample 35. Chase Palmer, analyst.

37. Brine from Fifth sand; depth 2,200 feet; well No. 1 of South Penn Oil Co., on Maggie McDonald farm, McDonald, Allegheny County, Pa. Production of water 1 or 2 barrels daily. S. C. Dinsmore, analyst. Reeves, Frank, op. cit., p. 374.

38. Brine from Peoples Natural Gas Co's. well, 8 miles southwest of Imperial, Washington County, Pa. Depth of well when sample was collected 6,300 feet. Geologic horizon believed to be that of Oriskany sandstone. The water rose 4,000 feet in the well. This water is remarkable for its very high content of strontium. George Steiger, analyst. U. S. Geol. Survey Water-Supply Paper 364, p. 9, 1914.

39. Water from a deep well on Slaughters Creek, near Coalburg, W. Va. The water is said to occur at a depth of 5,590 feet in a stratum of fine black sand whose geologic horizon is not reported. The water rose in the well about 3,000 feet. Sample collected in July, 1912, by William Seymour Edwards Oil Co., Charleston and Kanawha, W. Va. Chase Palmer, analyst. U. S. Geol. Survey Water-Supply Paper 364, p. 11, 1914.

## SHALLOW WELL WATERS.

The 15 analyses shown in Table 14 are selected from the files of the water-resources branch of the United States Geological Survey and represent waters from shallow wells in or near the areas studied during the preparation of this bulletin. Though all the analyses except No. 15 were made to show the quality of the water for use in boilers and are incomplete, they nevertheless afford a good idea of the character of the waters from the shallow rocks.

Ground waters of meteoric origin, such as are obtained from shallow wells, when percolating through soils and rocks near the surface take into solution various mineral constituents, so that the nature and proportions of the dissolved constituents depend largely on the kinds of rock with which the waters have been in contact. Calcium, magnesium, and carbonate are characteristic of waters in limestone areas. Sulphate is generally a derivative of surface oxidation. Sodium, whose reacting value exceeds the combined reacting values of chlorine and sulphate in the waters represented by analyses 2, 8, 9, and 15, has doubtless been derived from rocks rich in sodium-bearing minerals. Chlorine is present in all the waters analyzed and has been acquired either through the leaching of soluble chlorides from the shallow rocks or by the mixing of normal ground waters with chloride waters such as constitute the deep-seated brines.

The proportion of chlorine varies too much to warrant its use as a basis for extended comparison, but by comparing the analyses given in Table 14 with those given in Tables 8 to 13 a few broad differences between the shallow and deep waters are apparent. The proportions of total dissolved solids in the shallow waters are extremely diverse but are always smaller than in the deep-seated waters. All but one of the shallow waters contain a relatively large proportion of sulphate, and the reacting value of this constituent exceeds that of chlorine in each of the waters represented by analyses 1, 2, 3, 4, 11, 12, 13, and 14. The proportions of sulphate in the deep-seated brines are practically negligible. The shallow waters are characterized by a large proportion of carbonate, whereas that constituent is present in relatively small amount in the deep-seated waters. In all the shallow waters except the one represented by analysis 2 calcium exceeds magnesium. This relation also holds in the deep-seated waters, but the proportions of calcium and magnesium in the dissolved solids of the shallow waters are larger than in the deep-seated waters. In each of the shallow waters except those represented by analyses 3, 5, 6, and 10, the reacting value of sodium is either equal to or greater than that of chlorine. In the deep-seated brines the reacting values of sodium are less than those of chlorine.

A wide range of properties of reaction of the different shallow waters is shown in the lower part of Table 14. Primary salinity predominates in waters 5, 8, 10, and 15. The secondary chloride salinity of waters 3, 5, 6, and 10 indicates that these approach most nearly the deep-seated oil-field brines. Primary alkalinity is the predominating property of reaction in waters 2 and 9, and secondary alkalinity is the principal property of reaction in the waters represented by analyses 1, 3, 4, 7, 11, 12, 13, and 14. Though primary salinity predominates in the waters represented under analyses 8 and 15, the total properties of reaction of these two waters are also made up partly of primary alkalinity. ~~Primary alkalinity~~ in the deep-seated brines of the Appalachian fields is exceptional.

The large proportions of total dissolved solids, the relatively large proportions of chlorine with respect to sodium, and the comparatively small proportions of sulphate, due possibly to precipitation or reduction in the waters represented by analyses 5 and 15, lead to the conclusion that these waters are mixtures of waters from shallow and deep sources. Waters such as these, which are intermediate between normal ground waters and deep-seated brines, deserve further study than we have been able to give them. We have found it difficult to procure representative samples of such waters, which are unsatisfactory for industrial uses and are also generally excluded from deep wells by casings. It is probable, however, that studies of the waters accompanying oil in the shallow-sand territories of the Appalachian fields and of the waters immediately above and below the shallow oil sands would show, in places near the outcrops, evidences of the incursion of ground waters. The gradations from normal ground waters to characteristic deep-seated brines must depend partly on the extent to which the deeper waters have received accessions of shallow ground waters. In the succeeding pages we show some of the reactions that are involved when shallow ground waters of one type leak into oil wells and mix with deep-seated waters of a different type. We believe that similar changes have occurred in past geologic time, and this belief is strengthened by the fact that the reactions that would be produced by mixing and concentrating certain deep and shallow waters would bring about much the same difference that we observe between deep and shallow brines.

TABLE 14.—*Partial analyses of waters from shallow wells in the Appalachian oil and gas fields.*

**Milligrams per liter.**

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 113.7 | 6.4 | 26.2 | 58.5 | 223.1 | 38.8 | 28.6 | 15.9 | 5.0 | 19.0 | 11.7 | 80.2 | 66.3 | 95.6 | 50.0 |
| Mg | 20.7 | 7.2 | 4.3 | 17.0 | 84.5 | 13.5 | 5.2 | 3.5 | 2.8 | 6.7 | 5.6 | 20.9 | 11.7 | 12.3 | 10.0 |
| Na<br>K | 66.2 | 105.1 | 5.4 | 10.7 | 500.0 | 50.4 | 27.5 | 141.7 | 134.8 | 34.4 | 2.0 | 1.2 | 1.3 | 5.8 | 354.0 |
| Cl | 67.0 | 5.0 | 11.0 | 6.1 | 1,209.1 | 145.0 | 42.1 | 137.2 | 24.8 | 67.4 | 3.0 | 1.9 | 1.9 | 8.9 | 435.0 |
| SO$_4$ | 114.2 | 21.7 | 23.4 | 23.0 | 19.3 | 32.2 | 15.2 | 6.6 | 5.3 | 11.6 | 4.7 | 60.3 | 41.2 | 30.7 | ........ |
| HCO$_3$ | 365.5 | 298.4 | 67.3 | 252.0 | 325.1 | 29.3 | 93.4 | 196.4 | 337.2 | 43.9 | 58.0 | 272.8 | 209.3 | 314.1 | 261.0 |
| | 747.3 | 443.8 | 137.6 | 367.3 | 2,361.1 | 309.2 | 212.0 | 501.3 | 509.9 | 183.0 | 85.0 | 437.3 | 331.7 | 467.4 | 1,110.0 |

**Percentages of dissolved constituents.**

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 15.21 | 1.44 | 19.0 | 15.9 | 9.4 | 12.5 | 13.5 | 3.2 | 1.0 | 10.4 | 13.8 | 18.4 | 20.0 | 20.5 | 4.5 |
| Mg | 2.77 | 1.62 | 3.1 | 4.6 | 3.6 | 4.4 | 2.4 | .7 | .5 | 3.7 | 6.6 | 4.8 | 3.5 | 2.6 | .9 |
| Na<br>K | 8.86 | 23.7 | 3.9 | 2.9 | 21.2 | 16.3 | 13.0 | 28.3 | 26.5 | 18.8 | 2.4 | .2 | .4 | 1.2 | 31.9 |
| Cl | 8.97 | 1.1 | 8.0 | 1.7 | 51.2 | 46.9 | 19.9 | 27.3 | 4.9 | 36.8 | 3.5 | .4 | .6 | 1.9 | 39.2 |
| SO$_4$ | 15.28 | 4.9 | 17.0 | 6.3 | .8 | 10.4 | 7.2 | 1.3 | 1.0 | 6.3 | 5.5 | 13.8 | 12.4 | 6.6 | ........ |
| HCO$_3$ | 48.91 | 67.3 | 49.0 | 68.6 | 13.8 | 9.5 | 44.0 | 39.2 | 66.1 | 24.0 | 68.2 | 62.4 | 63.1 | 67.2 | 23.5 |
| | 100.00 | 100.00 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

**Reacting values, in per cent.**

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 27.7 | 2.9 | 34.5 | 30.5 | 14.0 | 18.5 | 23.5 | 5.5 | 2.0 | 16.6 | 25.8 | 34.7 | 38.2 | 39.6 | 7.1 |
| Mg | 8.3 | 5.4 | 9.3 | 14.7 | 8.7 | 10.6 | 6.9 | 1.9 | 1.8 | 7.2 | 20.4 | 14.9 | 11.1 | 8.3 | 2.3 |
| Na<br>K | 14.0 | 14.7 | 6.2 | 4.8 | 27.3 | 20.9 | 19.6 | 42.6 | 46.2 | 26.2 | 3.8 | .4 | .7 | 2.1 | 40.6 |
| Cl | 9.2 | 1.3 | 8.2 | 1.8 | 42.8 | 39.0 | 19.6 | 26.8 | 5.5 | 33.2 | 3.7 | .4 | .6 | 2.1 | 37.1 |
| SO$_4$ | 11.6 | 4.1 | 12.8 | 5.0 | .5 | 6.4 | 5.2 | .9 | .9 | 4.2 | 4.3 | 10.9 | 9.8 | 5.3 | None. |
| HCO$_3$ | 29.2 | 44.6 | 29.0 | 43.2 | 6.7 | 4.6 | 25.2 | 22.3 | 43.6 | 12.6 | 42.0 | 38.7 | 39.6 | 42.6 | 12.9 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

Properties of reaction, in per cent.

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Primary salinity | 28.1 | 10.8 | 12.4 | 9.6 | 54.6 | 41.8 | 39.2 | 55.5 | 12.8 | 52.4 | 7.6 | 0.9 | 1.4 | 4.1 | 74.2 |
| Secondary salinity | 13.5 | ........ | 29.6 | 4.0 | 32.0 | 16.4 | 10.5 | ........ | ........ | 22.4 | 8.4 | 21.8 | 19.4 | 10.6 | ........ |
| Primary alkalinity | ........ | 72.6 | ........ | ........ | ........ | ........ | ........ | 29.7 | 79.6 | ........ | ........ | ........ | ........ | ........ | 7.0 |
| Secondary alkalinity | 58.4 | 16.6 | 58.0 | 86.4 | 13.4 | 41.8 | 50.3 | 14.8 | 7.6 | 25.2 | 84.0 | 77.3 | 79.2 | 85.3 | 18.8 |
| | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

1. Water from Pittsburgh & Lake Erie Railroad Co.'s well at Pittsburgh, Pa. Analysis furnished by Kennicott Water Softening Co.
2. Water from Noulet well, Butler, Butler County, Pa. Analysis furnished by Baltimore & Ohio Railroad Co.
3. Water from Rifney well, New Castle Junction, Lawrence County, Pa. Analysis furnished by Baltimore & Ohio Railroad Co.
4. Water from a well 57 feet deep on Brown's farm, Venice, Washington County, Pa. Analysis furnished by Kennicott Water Softening Co.
5. Water from Leader Refining Co.'s well, Taylorstown, Washington County, Pa. Analysis furnished by Kennicott Water Softening Co.
6. Water from a shallow well at Milton, Cabell County, W. Va. Analysis furnished by Kennicott Water Softening Co.
7. Water from a shallow well at Eureka, Pleasant County, W. Va. Analysis furnished by Baltimore & Ohio Railroad Co.
8. Water from a driven well 100 feet deep at Smithfield, Wetzel County, W. Va. Analysis furnished by Baltimore & Ohio Railroad Co.
9. Water from a new shallow well at Littleton, Wetzel County, W. Va. Analysis furnished by Baltimore & Ohio Railroad Co.
10. Water from a new shallow well at Harris Ferry, Wood County, W. Va. Analysis furnished by Baltimore & Ohio Railroad Co.
11. Water from a well 48 feet deep on Cook farm, Harris Ferry, Wood County, W. Va. Analysis furnished by Baltimore & Ohio Railroad Co.
12. Water from an old shallow well at Holloway, Belmont County, Ohio. Analysis furnished by Baltimore & Ohio Railroad Co.
13. Water from a new shallow well at Holloway, Belmont County, Ohio. Analysis furnished by Baltimore & Ohio Railroad Co.
14. Water from a dug well at Belpre, Washington County, Ohio. Analysis furnished by Baltimore & Ohio Railroad Co.
15. Water from an artesian well about 350 feet deep on Neigh farm, Summit Township, Butler County, Pa. S. C. Dinsmore, analyst. This analysis is stated more completely in Table 9 (pp. 34–35).

## CHANGES IN OIL AND GAS FIELD WATERS AS DEDUCED FROM FIELD OBSERVATIONS AND CHEMICAL ANALYSES.

### MINERAL DEPOSITION DURING THE EXTRACTION OF OIL AND GAS.

The field observations and preliminary deductions upon which the studies outlined in this paper are largely based are here given in considerable detail.

The so-called salting up or clogging of gas wells by deposits of sodium chloride, a matter with which most petroleum geologists who have worked in the Appalachian fields are familiar, is a common cause of trouble to gas-well operators. Another cause of trouble that has not been generally recognized is the clogging of the productive sandstones themselves by the deposition of inorganic mineral matter in the rock interstices. During the field investigations in southeastern Ohio and western Pennsylvania preparatory for this report it was noted that tubings were pulled from oil and gas wells because newly deposited inorganic crusts had so caked the productive sands and the tubings of the wells as to interfere seriously with production. Pieces of sandstone that were shot and cleaned from old wells were crusted and impregnated with similar newly deposited materials.

Many instances of the "salting up" of gas wells were reported that could not be investigated, so that information on this subject has been partly obtained from operators. We are indebted to Mr. M. E. Lytle, of the Ohio Fuel Supply Co., for the following account of the deposition of salt in a gas well in Harrison Township, Knox County, Ohio. The well was drilled to the so-called Clinton sand, in which gas was encountered at a depth of about 2,700 feet. The sand was apparently dry of water, was 34 feet thick, and, under conditions of open flow, yielded gas at the rate of 6,800,000 cubic feet in 24 hours. The closed "rock pressure" was 810 pounds to the square inch. Tubing and pipe-line connections were put in at once, but, except for being blown off and tested with a pressure gage once a month, the well was not operated. Four months later gas from the well was turned into the pipe line, but within a day or so investigation proved that the well was "dead." Further investigation showed that the inside of the tubing was dry and free from obstructions clear to the bottom of the well. When the tubing was pulled out, salt water, which was said to have been previously excluded, leaked in from a shallow sand above the packer and partly filled the well. While this water was being bailed out, lumps of salt were found, and within 12 hours approximately 4,000 pounds of salt was cleaned from the well. Then some gas commenced flowing. Being satisfied that the Clinton sand was salted up, the operators lowered 40 quarts of nitroglycerin and exploded it at the productive horizon. This started gas flowing at the rate of 7,000,000 cubic feet in 24 hours and also ejected more salt. The well has been in constant use for 11 years and, though never clogged again, has continued to eject lumps of salt with the gas.

Under the conditions described it seems difficult to explain how great masses of salt could accumulate in the rocks at the bottom of the well or between the tubing and casing unless, during the time the well was not used, salt water leaked in from the Clinton or overlying sands and was exposed to the evaporative effects of expanding gas. This gas must have leaked, either to the surface or possibly from the Clinton sand into overlying beds in which lower gas pressures prevailed. Such movements of gas would cause the evaporation of relatively small quantities of salt water that might leak into the well.

Concerning a somewhat similar deposition of salt in a Clinton sand gas well Mr. Lytle wrote:

> In another well drilled by us, from which we used gas and which was watered with fresh water twice a week and allowed to stand three days out of six with water in it, the salt gradually formed in the tubing until it had very nearly filled 60 feet of 3-inch tubing and 300 feet of 2-inch. We were obliged to pull the packer and shoot this well. We have not had the tubing salt up since. This well has been producing for about 7 years.

Another striking example of the salting up of gas wells is reported by a field employee of the Ohio Fuel Supply Co. to have taken place in the Stumptown gas field, Wayne Township, Belmont County, Ohio. During the years 1905 to 1910 much natural gas was produced at this place from a sandy phase of the Maxville limestone (Big lime sand of Ohio, of late Mississippian age) at a depth of 1,250 feet. One of the wells here is reported to have yielded gas at the rate of 5,000,000 cubic feet a day when flowing openly, the initial rock pressure being approximately 440 pounds to the square inch. No salt water could be detected in the wells, but the operators observed that crusts of crystalline salt formed about the tubings at the productive horizon, so as to choke the wells and retard the flow of gas. Attempts were made to dissolve these salt incrustations by introducing fresh water into some of the wells and then pumping it out, but the pump valves at the bottoms of the wells became so rapidly clogged by salt as to interfere with this procedure. The fresh water that was introduced into the wells rapidly disappeared, and sometimes when the wells were allowed to "blow off" to remove the water and dissolved salt that could not be pumped out, fine particles of dry salt were ejected from the wells. It seems probable that the water with its dissolved salt was included in the gas as a spray and was evaporated into the relatively great volumes of expanding gas before reaching the top of the well, leaving only the particles of dry salt. In some of the fields where salting up of gas wells was reported the salt was successfully removed by introducing water into the wells and subsequently pumping off or blowing off the water with the dissolved salt.

At Barnesville, Warren Township, Belmont County, Ohio, Berea gas wells are also reported to have become salted up, and at one place near the Barnesville field crystalline salt, an analysis of which is given in Table 15, was collected from a gas line pressure regulator 4 to 7 miles from the wells that furnished the gas. Salt was deposited here in so large amounts that it became necessary to remove the accumulations once a year. It appears from this that particles of salt water were carried several miles in the form of a fine spray suspended in gas moving rapidly under pressure. On further expansion of the gas more complete evaporation of the water took place and crystalline salt was deposited. The interior of the regulator was sometimes observed to be wet. About 15,000,000 cubic feet of gas a month passed through this apparatus, in which the gas line pressure was reduced from 100 to 20 pounds to the square inch. Three-inch pipe lines were in use. Small amounts of salt water were pumped and blown off from the Berea gas wells at Barnesville, and water traps were used to remove water from the gas before it went into the pipe lines.

Salting up of gas wells at Cleveland, Ohio, is reported by G. S. Rogers,[1] who collected pieces of crystalline salts that formed in wells at the horizon of the so-called Clinton sand. This sand yields gas in the Cleveland field, but salt water, if present, can not be observed because of its evaporation into the gas. Rogers attributes the deposition of salt to the evaporation of salt water into expanding gas and thinks the water may leak to the Clinton sand from the higher lime sand (of early Devonian age; see stratigraphic table, p. 14), which is known to be water bearing.

We are indebted to Dr. I. C. White for an account of the deposition of salt in a gas well near Warfield, Ky. The well burned for about 20 years, during which the gas was not utilized. During that period the well occasionally became choked by salt, but when the gas pressure increased sufficiently the salt was blown from the well and the flow of gas began again as usual.

At Woodsfield, Center Township, Monroe County, Ohio, fragments of salt-incrusted Berea sandstone were collected as soon as they were bailed from an old oil well. On examination these specimens were found to contain 0.59 per cent by weight of salts soluble in water, of which 89.5 per cent by weight was sodium chloride. The well had been yielding oil together with a little gas and salt water for ten years prior to the collection of the incrusted fragments.

In this bulletin it is possible to cite only a few of the many examples of the deposition of salt in gas and oil wells. In addition to the examples above cited, we have received reports of similar phenomena in Butler, Lawrence, Beaver, Armstrong, and McKean counties, Pa., and Belmont, Monroe, Noble, Guernsey, Knox, Wayne, and Licking counties, Ohio. A few isolated cases in West Virginia have also been reported. The short time available has not permitted a more extensive investigation of the subject.

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[1] Rogers, G. S., The Cleveland gas field, Cuyahoga County, Ohio: U. S. Geol. Survey Bull. 661, pp. 19–20, 21, 31, 1917.

The salting up of gas wells is attributed largely to the evaporative effects of expanding gas, but under certain conditions chilling of deep-seated brines entering the wells is another cause of the deposition of salt. Where great volumes of highly compressed gas are allowed to escape through an open well or into low-pressure gas lines, the temperature of salt water accompanying the gas is probably lowered sufficiently to cause the deposition of salt.

Apparently the phenomenon is common in both oil and gas fields, though frequently it is not observed because of the very small amounts of salt deposited. In the Appalachian fields the salt content of specimens of the productive sands collected from oil wells is usually less than 1 per cent by weight, as is shown in Tables 1 and 3. The proportions of salt in specimens of pay sand from gas wells would doubtless be much greater. Analyses of some of the water-soluble salts collected during the studies relative to this paper are shown in Table 15.

TABLE 15.—*Analyses of water-soluble salt crusts collected from oil and gas wells.*

**Percentages by weight.**

| | 1 | 2 | 3 |
|---|---|---|---|
| Na | 38.70 | 35.2 | 38.82 |
| Ca | 0.15 | 3.4 | .09 |
| Mg | Trace. | .3 | None. |
| Fe | | | .04 |
| Cl | 59.80 | 60.2 | 59.92 |
| $SO_4$ | .18 | None. | .16 |
| $CO_3$ | None. | .9 | None. |
| Insoluble in $H_2O$ | .38 | | .32 |
| Organic matter | Present. | | Present. |
| | 99.21 | 100.0 | 99.35 |

**Conventional combinations calculated from the above figures, expressed as percentages by weight.**

| | 1 | 2 | 3 |
|---|---|---|---|
| NaCl | 98.37 | 89.5 | 98.64 |
| $CaCl_2$ | .20 | 7.6 | .14 |
| $MgCl_2$ | Trace. | 1.3 | None. |
| $FeSO_4$ | | | .11 |
| $CaSO_4$ | .26 | | .14 |
| $CaCO_3$ | | 1.6 | |
| Insoluble in $H_2O$ | .38 | | .32 |
| Organic matter | Present. | | Present. |
| | 99.21 | 100.0 | 99.35 |

1. Salt crust, 98.83 per cent soluble in water, from a Clinton sand gas well, Cleveland, Ohio. Collected by G. S. Rogers. R. C. Wells, analyst.
2. Water-soluble portion of Berea sand from an oil well 10 years old, Woodsfield, Center Township, Monroe County, Ohio, representing 0.59 per cent of the sand. R. C. Wells, analyst.
3. Salt crust, 99.03 per cent soluble in water, collected from a gas-pressure regulator between 4 and 7 miles from the Berea wells that yielded gas together with water from which the salt was deposited, Barnesville, Belmont County, Ohio. R. C. Wells, analyst.

A few examples of the deposition of inorganic substances other than soluble chlorides may be of interest. In Forward Township, Butler County, Pa., fragments of a crust consisting of barium sulphate, with strontium and calcium sulphates, ferric oxide, and soluble chlorides, as shown by analysis 3, Table 16, were collected from an old oil well. The well had been yielding oil and salt water for about 15 years and had become badly fouled by mineral incrustations, when it was shot and cleaned. Angular fragments of the crust, 2 inches wide and half an inch thick, containing included globules of gelatinous hydrocarbons, were then collected. The crusts were formed at the horizon of the productive bed (Third sand, depth 1,470 feet).

A deposit of barium sulphate and calcium carbonate in an oil well was also observed in Butler Township, Butler County, Pa., where the bottom portion of the tubing of a well was found to be so incrusted with these substances as to close most of the intake perforations completely, practically stopping production from the well. Only the bottom length of the tubing, the part which was immersed in salt water and oil, was incrusted. The well yielded oil and salt water from the Hundred-foot sand at a depth of 1,380 feet. In this well the deposition of calcite upon the tubing had been followed by that of barium sulphate, which had, in turn, been followed by further deposition of calcite. The resultant banded nature of the crust is shown by Plate IV (p. 52). It is interesting to note that the crusts were so deposited upon surfaces wet with oil and water as to exclude both oil and water from the intake perforations. The well was double-cased halfway through the Hundred-foot sand, and the operators claimed that afterward practically no water leaked in from beds above the Hundred-foot sand.

The coarsely crystalline texture of the barium sulphate crusts indicates slow deposition, but the causes for this deposition in oil wells are uncertain. Among the possible causes may be mentioned the mixing in the wells of dilute solutions of soluble barium salts with solutions containing soluble sulphates. It seems probable that notwithstanding the agitation of the solutions at the productive horizons in the oil wells the precipitation of barium sulphate must have been slow, because of the very dilute solutions of sulphates and soluble barium salts involved. Siebenthal[1] has quoted Carles's work[2] to show that some barium may remain in solution in the presence of some sulphate in bicarbonate waters. It may be that in these oil-field waters, particularly where bicarbonate waters leak into the wells from rocks near the surface, the breaking down of bicarbonates, due to the loss of carbon dioxide from solution, together with other gases, facilitates the slow deposition of barium sulphate. This mode of

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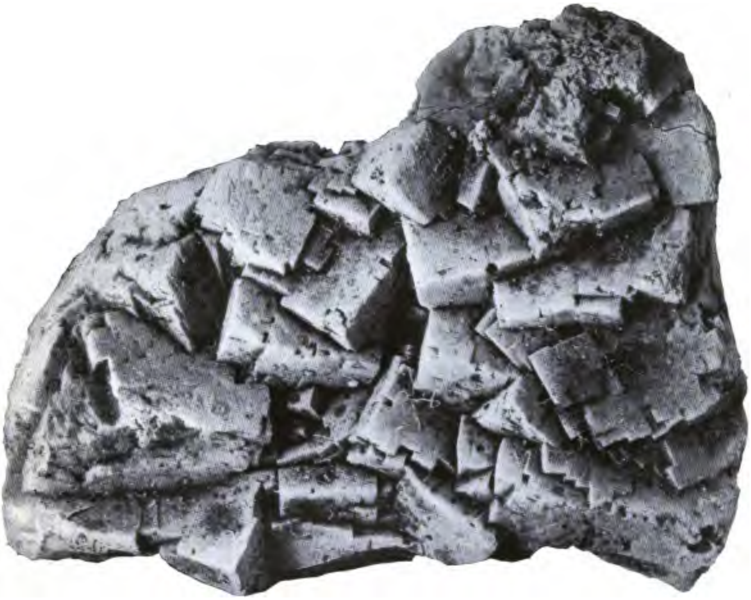
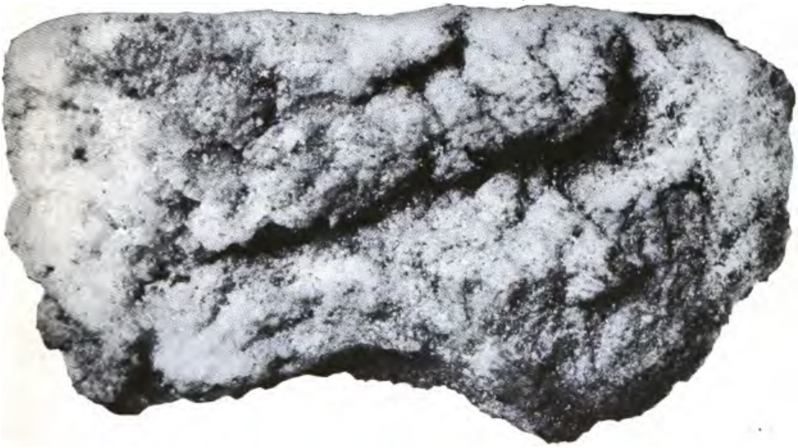
[1] Siebenthal, C. E., Origin of the zinc and lead deposits of the Joplin region, Missouri, Kansas, and Oklahoma: U. S. Geol. Survey Bull. 606, pp. 55–56, 1915.

[2] Carles, M. P., Présence de la baryte dans les eaux minérales sulphatées: Annales chim. anal., vol. 7, pp. 91–93, 1902.



*A.* FRAGMENT OF SALT CRUST FROM A CLINTON SAND GAS WELL, CLEVELAND, OHIO.

Collected by G. S. Rogers. The composition of the crust is shown by analysis 1, Table 15.



*B.* FRAGMENT OF SALT CRUST AT BARNESVILLE, OHIO.

Collected for the authors by a field employee of the Ohio Fuel Supply Co. The salt was deposited in a gas-line pressure regulator situated between 4 and 7 miles from the Berea wells supplying the gas. The composition of the crust is shown by analysis 3, Table 15.

SALT CRUSTS FORMED DURING THE PRODUCTION OF NATURAL GAS.

Photographs three times natural size.

slow deposition is suggested by the uniform thickness and coarsely crystalline texture of the crusts and also by the admixture of barium sulphate with calcium carbonate, which would be precipitated as a carbonate on the loss of carbon dioxide from bicarbonate solutions.

Calcium carbonate, magnesium carbonate, and ferrous carbonate are deposited on tubings, on the walls of the wells, and in the interstices of productive sands. The carbonate deposits are most commonly found in the bottoms of old oil wells, though some carbonates are believed to be deposited in the interstices of the sands at considerable distances from the producing wells. This inference has been suggested by the petrographic and chemical examination of a large number of mineral crusts and specimens of oil and gas bearing sandstones collected from both old and new wells. Analyses of a few of these carbonate deposits are given in Table 16. The photographs reproduced in Plates II. III. and IV illustrate the mode of occurrence of the crusts.

TABLE 16.—*Analyses of mineral crusts collected from oil wells.*

**Percentages by weight.**

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Soluble in water[a] | 0.10 | 0.11 | 0.34 | 0.47 | .......... |
| FeO | .53 | .69 | .......... | .32 | .......... |
| $Fe_2O_3$ | .27 | .20 | .11 | 3.63 | 0.60 |
| BaO | .......... | .......... | [b] 61.07 | .......... | 56.71 |
| CaO | 53.37 | 53.08 | .81 | 1.44 | 4.41 |
| SrO | .16 | .46 | 1.61 | .......... | .......... |
| MgO | .60 | .49 | .......... | .18 | .12 |
| $CO_2$ | 42.98 | [c] 43.17 | Trace. | 1.32 | 2.33 |
| $SO_3$ | .......... | .......... | 34.29 | .17 | 31.85 |
| $SiO_2$ | .......... | .......... | .......... | 91.69 | 2.12 |
| Organic matter and moisture | .......... | .......... | .......... | .97 | .......... |
| | 98.01 | 98.20 | 98.23 | 100.19 | 98.14 |

**Revised analyses.**

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Soluble in water[a] | 0.10 | 0.11 | 0.34 | 0.47 | .......... |
| $Fe_2O_3$ | .27 | .20 | .11 | 3.63 | 0.60 |
| $CaCO_3$ | 95.27 | 94.90 | Trace. | 2.30 | 5.00 |
| $SrCO_3$ | .23 | .65 | .......... | .......... | .......... |
| $MgCO_3$ | 1.33 | 1.08 | .......... | .20 | .25 |
| $FeCO_3$ | .86 | 1.11 | .......... | .52 | .......... |
| $BaSO_4$ | .......... | .......... | 92.95 | .......... | 86.26 |
| $SrSO_4$ | .......... | .......... | 2.86 | .......... | .......... |
| $CaSO_4$ | .......... | .......... | 1.97 | .29 | 3.91 |
| CaO | .......... | .......... | .......... | [d] .03 | .......... |
| MgO | .......... | .......... | .......... | [d] .09 | .......... |
| $SiO_2$ | .......... | .......... | .......... | 91.69 | 2.12 |
| Organic matter and moisture | [e] 1.99 | [e] 1.80 | [e] 1.77 | .97 | .......... |
| | 100.05 | 99.85 | 100.00 | 100.19 | 98.14 |

[a] Essentially sodium chloride.
[b] Calculated for $SO_3$. Presence proved by qualitative tests.
[c] Calculated to satisfy bases.
[d] Probably present as silicate.
[e] By difference.

1. Crust cleaned from tubing of an old well yielding oil and salt water from the Hundred-foot sand, Summit Township, Butler County, Pa. The depth at which the crust formed is not known. The sample was collected from the derrick floor after the tubings had been cleaned. R. C. Wells, analyst.
2. Crust cleaned from tubing of an old oil well yielding oil and salt water from the Hundred-foot sand, Summit Township, Butler County, Pa., about a quarter of a mile from well where sample 1 was collected. The sample was collected from derrick floor after well tubings had been cleaned. R. C. Wells, analyst.
3. Crust cleaned from the bottom of a well that had been yielding oil and salt water from the Third sand for about 15 years, 1 mile northeast of Water Station, Forward Township, Butler County, Pa. R. C. Wells, analyst.
4. Incrusted fragments of sandstone cleaned from the bottom of an old well that had been idle for about 15 to 18 years, Evans City, Butler County, Pa. The well had formerly yielded oil and salt water from the Hundred-foot sand. R. C. Wells, analyst.
5. Crust (see B, Pl. IV) collected from the bottom part of the tubing of an old well yielding oil, gas, and salt water from the Hundred-foot sand, Butler Township, Butler County, Pa. S. C. Dinsmore, analyst.

The deposition of carbonates seems to be caused partly by the leaking into the wells and mixing of carbonate waters from shallow rocks with the deep-seated brines. When such waters are mixed and subsequently undergo concentration, any sodium bicarbonate in the shallow water will react with the calcium chloride of the deeper water to form calcium carbonate, sodium chloride, carbon dioxide, and water, according to the reaction

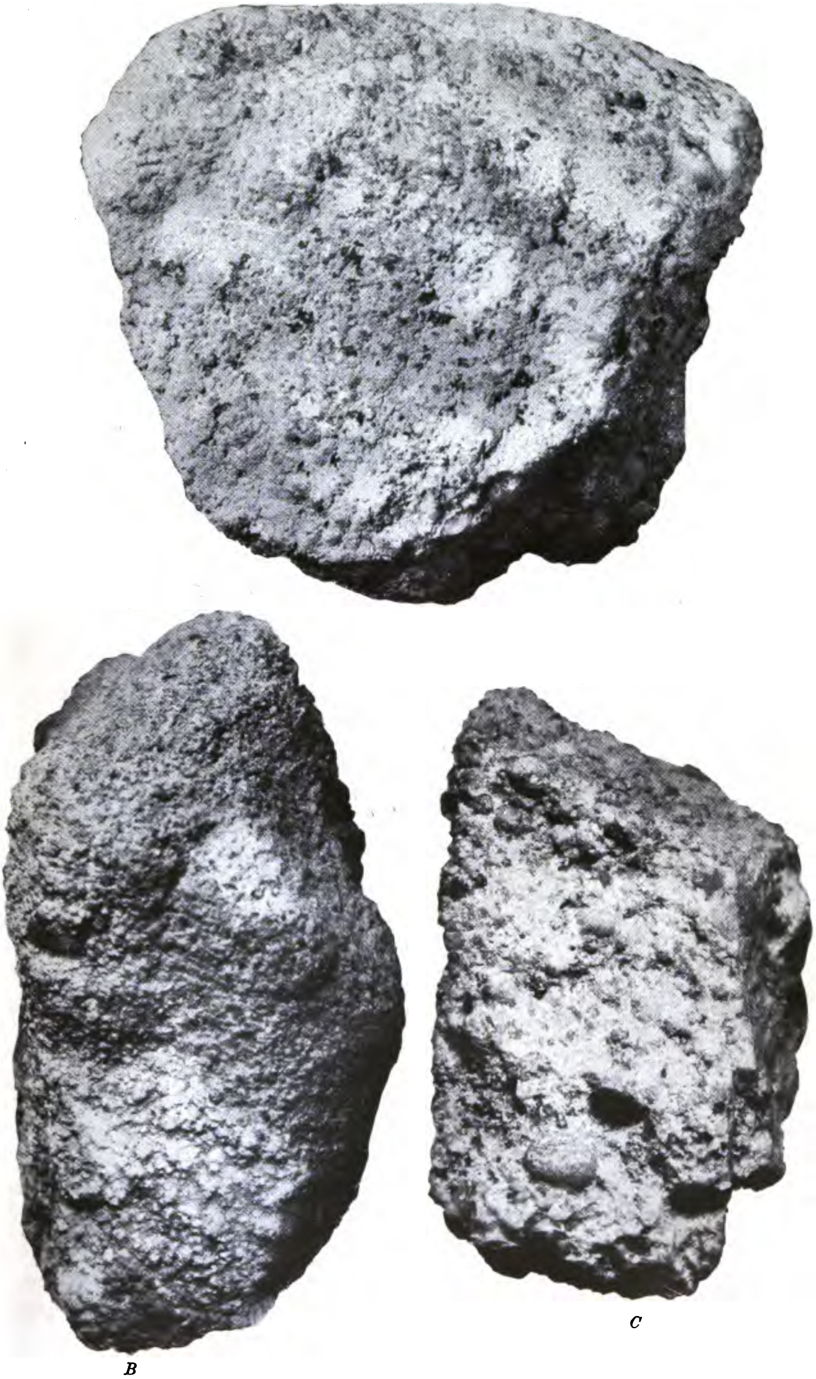
$$2\ NaHCO_3+CaCl_2=CaCO_3+2\ NaCl+CO_2+H_2O$$

In this connection it is important to note the presence of sodium chloride in the carbonate crusts from old oil and gas wells, and also the fact that calcium carbonate crusts in such wells are particularly abundant in Butler County, Pa., where some of the waters of the shallow rocks contain sodium in excess of the strong acid radicles and therefore have primary alkalinity. The decrease in the solubility of calcium carbonate in the presence of increasing proportions of calcium chloride is also a probable factor in the formation of these deposits, especially where waters that have dissolved calcium carbonate become mixed with the deep-seated waters. Another cause for the deposition of carbonates is the previously mentioned breaking down of soluble bicarbonates due merely to the liberation of carbon dioxide, together with other gases, from solution in water. In all these processes the concentration of the waters due to the removal of water vapor in the escaping natural gases is believed to play an important part.

## CHANGES IN THE DEEP-SEATED WATERS DURING THE EXTRACTION OF OIL AND GAS.

### METHOD OF STUDY.

The partial removal of some of the dissolved constituents from the waters necessarily results in changes in the proportions of the remaining constituents. In order to understand these changes as fully as possible and to correlate the evidence furnished by the deposition of mineral matter just described, we compared analyses of water collected at different periods of production from the initial well in a new oil and gas field. Similar comparisons were also made between waters from the same geologic horizon in old and new fields and between waters from different horizons in the same or neighboring fields. These comparisons have resulted in the discovery of certain general relations between the changes in the waters during the extraction of oil and gas by man and the natural changes that have taken place during the lapse of geologic time.



INCRUSTED SANDSTONE, IMPREGNATED BY CARBONATES, FROM OLD OIL WELLS NEAR EVANS CITY, BUTLER COUNTY, PA.

*A*, Collected by R. Van A. Mills, Hundred-foot sand, depth 1,060 feet. *B*, Collected by a field employee of the South Penn Oil Co., Hundred-foot sand, depth 1,050 feet. *C*, Transverse section of *B*, showing interstitially deposited carbonates as white patches. All photographs three times natural size.

### COMPARISON OF WATERS FROM THE SAME WELL.

Analyses of water from the Keener sand, Miltonsburg, Monroe County, Ohio, collected from the same well at different periods of production are shown in Table 17, and some of the conditions of production are indicated in figure 4. It is evident that the proportion of total dissolved solids in the waters collected from the same well increased as production continued. Moreover, the analyses indicate changes in the relative proportions of the different constituents, the ratio of calcium to chlorine being greater and the ratio of sodium ~~to chlorine being smaller~~ in the more concentrated water. Of the changes involved that in concentration is the most pronounced. We believe that such a change would be noted in waters from practically all initial wells in new fields where infiltrating waters are excluded

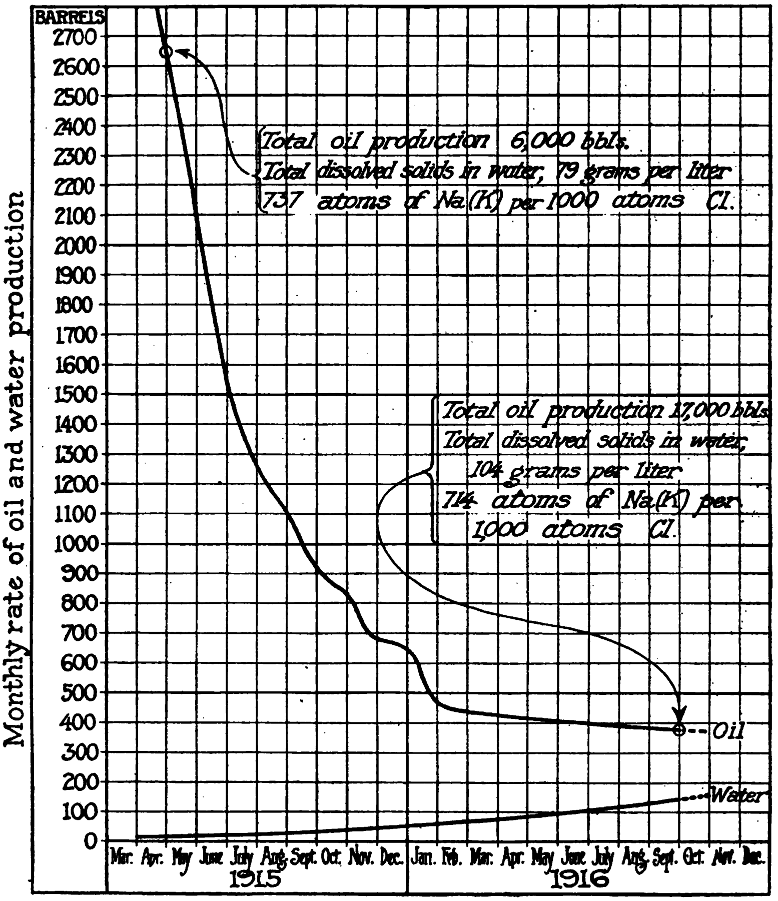


FIGURE 4.—Curve showing the rates of production of oil and water from well No. 1, Schroeder heirs' farm, Miltonsburg, Malaga Township, Monroe County, Ohio, when water samples were collected from that well.

and there is a noteworthy escape of gas. This belief is based partly on our numerous comparisons of waters from the same sands in new and old fields where gas was being extracted.

TABLE 17.—*Analyses of brine collected at different periods of production from Keener sand in well No. 1, Schroeder heirs' farm, Miltonsburg, Ohio.*

[Depth of sand 1,465 to 1,471 feet. This was the initial well in a new oil and gas field. Analyses in grams per liter.]

| | 1 | 2 |
|---|---|---|
| $SiO_2$ | 0.08 | 0.04 |
| Fe | .01 | ........ |
| Al | .36 | ........ |
| Ca | 5.68 | 8.34 |
| Mg | 1.04 | 1.48 |
| Na | 22.84 | 29.74 |
| K | .60 | |
| $CO_3$ | None. | None. |
| $HCO_3$ | .08 | .03 |
| $SO_4$ | None. | None. |
| Cl | 48.46 | 64.10 |
| | 79.15 | 103.73 |
| Ca÷Cl | .117 | .130 |
| Na÷Cl | .471 | .464 |

1. Collected April 24, 1915, when the well was 1 month old. S. C. Dinsmore, analyst. Gas, oil, and water were flowing from the well. The approximate rate of production at that time is shown by figure 4.

2. Collected when the well was 18 months old. Chase Palmer, analyst. The gas pressure had declined and the well had ceased to flow. The rate of production of oil had declined and the rate of production of water had increased, as shown by figure 4.

Several explanations may be offered to account for the changes noted. It is believed that the evaporation of water into the escaping gas is the principal cause for the change in concentration. Another possible explanation is that the more concentrated water comes from a part of the sand where the water has undergone advanced concentration either prior to drilling or in an older oil and gas field. The suggestion that the changes in concentration are related to the extraction of gas is strengthened by the fact that water from certain deep wells where oil and gas are practically absent has shown for many years no significant change in character or concentration.[1]

No single explanation for the changes other than that of concentration can be advanced without reservation. It will be understood, for instance, that the changes in the relative proportions of the dissolved constituents may be accounted for by the leakage into the wells of carbonate waters having primary alkalinity. The reaction that is involved when such waters are mixed with the deep-seated brines and subsequently concentrated has been briefly described on page 50. Relatively little sodium chloride is lost from the solution, but both calcium and magnesium are deposited as carbonates. This pre-

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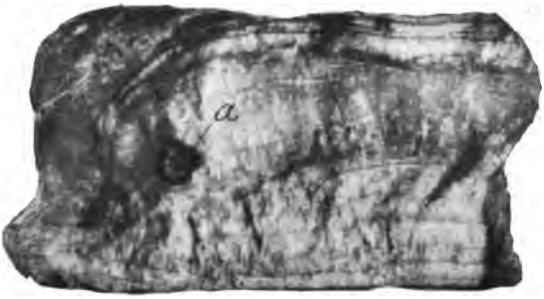
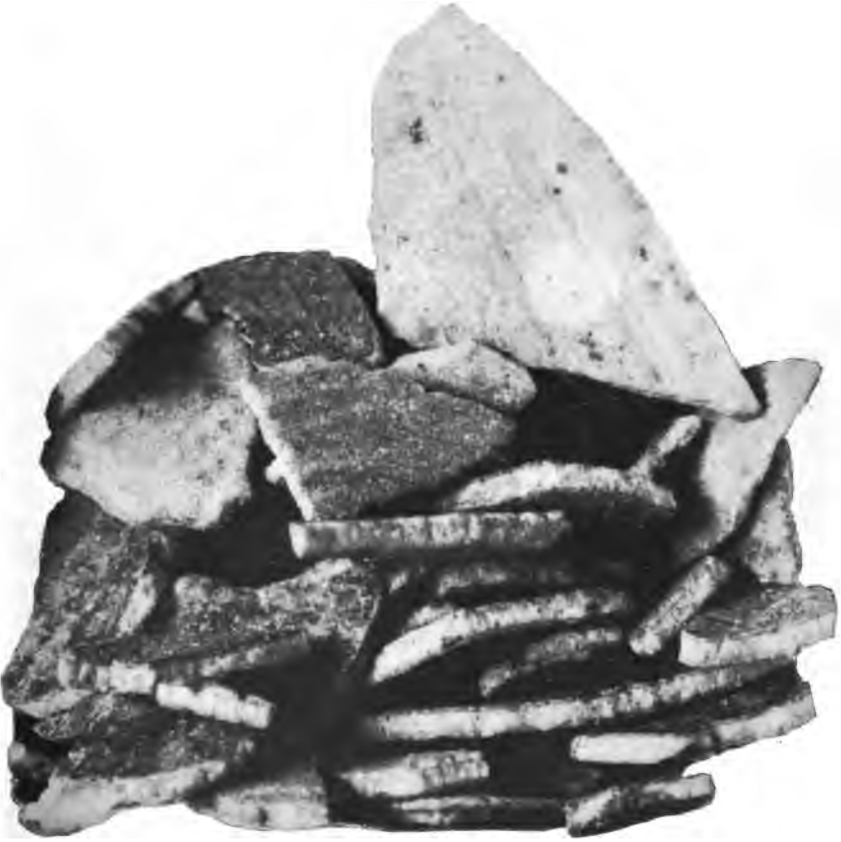
[1] Bownocker, J. A., Salt deposits and the salt industry in Ohio: Ohio Geol. Survey, 4th ser., Bull. 8, p. 27, 1906.

Stephenson, L. W., and Palmer, Chase, A deep well at Charleston, S. C., with a report on the mineralogy of the water: U. S. Geol. Survey Prof. Paper 90, p. 90, 1914.



*A*. FRAGMENTS OF A SULPHATE CRUST.

Collected for the writers by J. C. Mettler, Evans City, Pa. The deposit was cleaned from an old well that had been yielding oil and salt water from the Third sand (probably Upper Devonian) for about 15 years. Locality, 1 mile northeast of Water station, Forward Township, Butler County, Pa. The dark mass (*a*) is a soft waxy hydrocarbon that is included in the crust. The composition of the deposit is shown by analysis 3, Table 16. Photograph three times natural size.



*B*. FRAGMENT OF A MIXED SULPHATE AND CARBONATE CRUST FROM THE BOTTOM PART OF THE TUBING OF AN OLD WELL YIELDING OIL, GAS, AND SALT WATER FROM THE HUNDRED-FOOT SAND, BUTLER TOWNSHIP.

Collected by R. Van A. Mills. Petrographic examination has shown that the specimen consists essentially of barite and calcite in alternate layers. Small amounts of sodium chloride are also present. The calcite and barite crystals are slightly interlocked in comblike structure.

SULPHATE CRUSTS FROM OIL WELLS IN BUTLER COUNTY, PA.

cipitation tends to bring about differences in the sodium-chlorine and calcium-chlorine ratios, such as have been noted. Furthermore the extensive occurrence in the sands of secondary carbonates containing small proportions of sodium chloride indicates changes of this type.

The deposition of sodium chloride, with possibly very minor amounts of calcium and magnesium chlorides, during the concentration of the water would also cause such changes in the relative proportions of the dissolved constituents as are actually noted. The occurrence of deposits of sodium chloride in gas wells and in the interstices of the productive rocks indicates this mode of change in many fields.

To ascertain, approximately, the dissolved constituents that may be lost from the brines during concentration so as to cause the differences shown in Table 17, we have made further comparisons of the analyses in that table, and the results are set forth in Table 18. Here the analyses are simplified by rejecting the minor constituents and by slightly altering the values for sodium until an exact balance between the bases and chlorine is obtained so that the dissolved constituents can be expressed as chlorides. The analyses are given under 1 and 2 respectively. The values in column 1a are obtained by multiplying those in column 1 by an arbitrary factor (1.482), which is equivalent to making a hypothetical concentration of the more dilute water to 67.48 per cent of its original volume. This hypothetical concentration has been selected in order that the calcium content of water 1a and water 2 should be approximately the same. Calcium chloride, being more soluble than sodium chloride, would not be expected to deposit with sodium chloride at first; nevertheless small amounts of calcium and magnesium chloride seem to accompany the sodium chloride actually found in the oil and gas bearing rocks, so that the hypothetical concentration has been carried to a point to yield a slight excess of calcium chloride. No error is thus introduced, inasmuch as the results more nearly agree with conditions actually noted. Moreover, if the hypothetical concentration of the dilute water should be varied slightly in either direction, the hypothetical salt deposit would still approximate the salt deposits found in the reservoir rocks, sodium chloride being the predominating constituent.

It will be seen from Table 18 that the difference in the salt contents of the waters under comparison is expressed essentially as one of sodium chloride. It will also be noted that the composition of the salts hypothetically removed from the dilute water during its concentration agrees closely with the composition of natural salt deposits and with that of salt crusts collected from wells. The comparison therefore furnishes further evidence that the change in the waters may be due to the loss of sodium chloride during the concentration of the water accompanying the extraction of oil and gas.

**TABLE 18.**—*Analyses illustrating the probable loss of sodium chloride from solution during the concentration of a Keener brine issuing from the initial well in a new field near Miltonsburg, Ohio.*

[The figures given under 1 and 2 in this table have been recalculated from analyses 1 and 2, Table 17.]

| | 1 | 1a | 2 | 3 | |
|---|---|---|---|---|---|
| | *Grams per liter.* | *Grams per liter.* | *Grams per liter.* | *Grams (1a—2).* | *Per cent.* |
| $CaCl_2$ | 15.76 | 23.36 | 23.13 | 0.23 | 1.76 |
| $MgCl_2$ | 4.08 | 6.04 | 5.81 | .23 | 1.76 |
| NaCl | 57.39 | 86.78 | 74.16 | 12.62 | 96.48 |
| KCl | 1.14 | | | | |
| | 78.37 | 116.18 | 103.10 | 13.08 | 100.00 |

1. Simplified analysis of water collected when the well was one month old. Gas, oil, and water were flowing from the well. The approximate rates of oil and water production are shown by figure 4 (p. 51).

1a. Same water as 1, hypothetically concentrated to 67.48 per cent of its original volume (factor 1.482).

2. Simplified analysis of water collected when the well was 18 months old. During the interval between the collecting of samples 1 and 2 large amounts of gas and oil had been produced from this and neighboring wells. The changes in the rates of production of oil and water from the well are shown by figure 4.

3. Approximately the weights and relative proportions of the salts whose removal from 1.482 liters of water 1 together with evaporation would yield 1 liter of water 2.

From another point of view, however, it is well to note that the differences between the dissolved solids in the waters under comparison can be expressed merely as the differences between columns 1 and 2 in Table 18. One liter of the more concentrated water whose dissolved constituents are represented in column 2 may be considered as having formed through the introduction into an equal volume of the more dilute water of 7.37 grams of calcium chloride, 1.73 grams of magnesium chloride, and 15.63 grams of sodium and potassium chlorides. This implies an accession to the formerly dilute water of salts consisting of 29.80 per cent of calcium chloride, 7 per cent of magnesium chloride, and 63.20 per cent of sodium and potassium chlorides. These salts are too soluble to have remained undissolved in water such as first issued from the well and were therefore not acquired by simple leaching during the extraction of oil and gas. It is possible, however, that waters containing relatively large proportions of calcium chloride may have gained access to the well from various sources as the extraction of oil and gas proceeded. As water is drawn from a sandstone reservoir more or less water doubtless percolates into the sand from the surrounding rocks. Water from shales and other argillaceous strata might contain a relatively large proportion of calcium derived through the exchange of sodium in the brines for calcium in the reactive minerals of the shales. The nature of the reactions involved is discussed on page 75. The entrance of such waters into the sands, with or without concentration, may thus account for the changes in the waters noted during the extraction of oil and gas. The comparison of the waters can thus be made on the basis of changes of either type. We retain the comparison in terms of the loss of sodium, because it is sufficient for the purpose in view and because it also expresses the changes that occur when the waters are concentrated to the point of deposition of sodium chloride.

### COMPARISONS OF WATERS FROM THE SAME GEOLOGIC HORIZONS IN NEIGHBORING FIELDS.

From numerous detailed comparisons between the dissolved constituents of waters collected from the same sands in neighboring fields Tables 19 and 20 have been compiled to illustrate the evidence thus obtained. In general, the more concentrated waters occur in the older fields. Also, with but few exceptions, the ratio of calcium to chlorine is greater and the ratio of sodium to chlorine is smaller in the more concentrated waters. Furthermore, it is shown that almost invariably the concentration of the more dilute water, together with the removal of dissolved constituents consisting essentially of sodium chloride, would yield the more concentrated water. Again, the salts whose removal from solution can thus be postulated agree in composition closely with the salts from wells and with natural deposits of chloride salts. The differences between the more dilute and more concentrated waters in the same sand are of practically a uniform type, no matter whether the waters are drawn from a single well at different stages in its operation or from neighboring fields where the conditions of production have been widely different.

TABLE 19.—*Comparison of analyses of two waters from the Big lime sand showing the constituents whose removal from the more dilute water, together with evaporation, would yield the more concentrated water.*

[Samples collected from different fields 4½ miles apart in the northern part of Monroe County, Ohio.]

| | 1 | 1a | 2 | 3 | |
|---|---|---|---|---|---|
| | *Grams per liter.* | *Grams per liter.* | *Grams per liter.* | *Grams* (1a—2). | *Per cent.* |
| $SiO_2$ | 0.02 | 0.04 | 0.09 | —0.05 | .......... |
| Fe | .08 | .17 | .02 | .15 | 0.43 |
| Ca | 5.58 | 12.00 | 11.56 | .44 | 1.27 |
| Mg | 1.04 | 2.24 | 1.83 | .41 | 1.19 |
| Na | 23.86 | 51.30 | 39.27 | 12.03 | 34.82 |
| K | .25 | .54 | .69 | — .15 | .......... |
| $HCO_3$ | .32 | .69 | .03 | .66 | 1.91 |
| Cl | 50.40 | 108.36 | 87.50 | 20.86 | 60.38 |
| | 81.55 | 175.34 | 140.99 | 34.35 | 100.00 |
| Ca+Cl | 0.111 | .......... | 0.132 | .......... | .......... |
| Na+Cl | .473 | .......... | .449 | .......... | .......... |

**Weights and proportions of compounds whose removal from 2.150 liters of water 1, together with evaporation, would yield 1 liter of water 2.**

[Recalculated from No. 3, above.]

| | Grams. | Per cent. |
|---|---|---|
| $CO_2$ | 0.24 | 0.70 |
| $H_2O$[a] | .10 | .29 |
| $FeCO_3$ | .31 | .91 |
| $CaCO_3$ | .20 | .58 |
| $CaCl_2$ | 1.00 | 2.90 |
| $MgCl_2$ | 1.61 | 4.66 |
| NaCl | 31.09 | 89.96 |
| KCl | .......... | .......... |
| $CaSO_4$ | .......... | .......... |
| | 34.55 | 100.00 |

[a] This represents only the water from bicarbonates, a very small amount in comparison with the water lost by evaporation.

1. Brine collected September 15, 1916, from Big lime sand; depth 1,339 to 1,349 feet; new gas well in a new oil and gas field near Miltonsburg, Malaga Township, Monroe County, Ohio. Specific gravity of the water 1.0559. R. C. Wells, analyst.

1a. Same water as No. 1, hypothetically concentrated to 46.51 per cent of its original volume (factor 2.150).

2. Brine collected April 24, 1915, from Big lime sand; depth 1,431 to 1,444 feet; from an old oil and gas field in the northeastern part of Malaga Township, Monroe County, Ohio, near Jerusalem village. S. C. Dinsmore, analyst.

3. Approximately the weights and relative proportions of the constituents whose removal from 2.150 liters of water 1, together with evaporation, would yield 1 liter of water 2.

TABLE 20.—*Comparison of analyses of two waters from the Keener sand showing the constituents whose removal from the more dilute water, together with evaporation, would yield the more concentrated water.*

[Samples collected from different fields 7½ miles apart in the northern part of Monroe County, Ohio.]

| | 1 | 1a | 2 | 3 | |
|---|---|---|---|---|---|
| | *Grams per liter.* | *Grams per liter.* | *Grams per liter.* | *Grams* (1a—2). | *Per cent.* |
| $SiO_2$ | 0.05 | 0.20 | 0.08 | 0.12 | 0.11 |
| Fe | .01 | .14 | .......... | .04 | .04 |
| Ca | 2.98 | 11.62 | 11.36 | .26 | .24 |
| Sr | .08 | .31 | .......... | .31 | .28 |
| Mg | .83 | 3.24 | 1.63 | 1.61 | 1.47 |
| Na | 19.84 | 77.38 | 38.32 | 39.06 | 35.67 |
| K | .23 | .90 | .51 | .39 | .36 |
| $HCO_3$ | .17 | .66 | .03 | .63 | .57 |
| Cl | 38.92 | 151.79 | 84.71 | 67.08 | 61.26 |
| | 63.11 | 246.14 | 136.64 | 109.50 | 100.00 |
| Ca+Cl | .076 | .......... | .134 | .......... | .......... |
| Na+Cl | .510 | .......... | .452 | .......... | .......... |

TABLE 20.—*Comparison of analyses of two waters, etc.*—Continued.

**Weights and proportions of compounds whose removal from 3.900 liters of water 1, together with evaporation, would yield 1 liter of water 2.**

[Recalculated from No. 3, p. 56.]

| | Grams. | Per cent. |
|---|---|---|
| $SiO_2$ | 0.12 | 0.11 |
| $CO_2$ | .23 | .21 |
| $H_2O$[a] | .09 | .08 |
| $FeCO_3$ | .08 | .07 |
| $CaCO_3$ | .42 | .38 |
| $CaCl_2$ | .47 | .42 |
| $MgCl_2$ | 6.29 | 5.75 |
| NaCl | 101.05 | 92.30 |
| KCl | .75 | .68 |
| | 109.50 | 100.00 |

[a] This represents only the water from bicarbonates, a very small amount in comparison with the water lost by evaporation.

1. Brine from Keener sand; depth, 1,302 feet; sample collected November 7, 1916, from a new oil well in a new field near Monroefield, Malaga Township, Monroe County, Ohio. Very little gas was produced in this field. Specific gravity of the water 1.0437. R. C. Wells, analyst.

1a. Same water as No. 1, hypothetically concentrated to 25.64 per cent of its original volume (factor 3.900).

2. Brine from Keener sand; depth, 1,451 to 1,469 feet; sample collected April 24, 1915, from an old oil and gas well in an old oil and gas field near Jerusalem Village, Sunsbury Township, Monroe County, Ohio. S. C. Dinsmore, analyst.

3. Approximately the weights and relative proportions of the constituents whose removal from 3.900 liters of water 1, together with evaporation, would yield 1 liter of water 2.

## EVIDENCE THAT SIMILAR DIFFERENCES IN THE WATERS HAVE BEEN BROUGHT ABOUT DURING GEOLOGIC TIME.

### COMPARISON OF WATERS FROM DIFFERENT GEOLOGIC HORIZONS.

In the foregoing text we have presented evidence that changes in the waters under scrutiny occur during the extraction of oil and gas from the reservoir rocks. The changes are indicated by differences in concentration, differences in the relative proportions of the dissolved constituents, the apparent loss of certain constituents from solution, and the possible accession of other constituents. It appears, however, that such changes are not only closely related to the extraction of oil and gas but have also occurred from natural causes during geologic time.

As evidence bearing on this subject we submit in Tables 21, 22, and 23 comparisons of waters collected from beds at different geologic horizons in the same and neighboring fields. The waters under comparison in each table have been subjected to the effects of oil and gas production for approximately equal periods of time, the conditions of production being nearly the same, but nevertheless the waters show marked differences in concentration as well as in the proportions of their dissolved constituents. These differences are practically the same as those which appear to be brought about under the various conditions of oil and gas extraction by man. We are therefore led to ascribe them to the same causes. The more concentrated solutions have probably been concentrated, owing to evaporation into expanding gas which has removed more water than has been lost from the dilute solutions. We shall next attempt, therefore, to examine the evidence of the natural escape of gas that might afford conditions for concentration and changes in the waters similar to those brought about during the extraction of oil and gas.

**Table 21.**—*Comparison of analyses of two gas-field waters from different geologic horizons, showing the constituents whose removal from the more dilute water, together with evaporation, would yield the more concentrated water.*

| | 1 | 1a | 2 | 3 | |
|---|---|---|---|---|---|
| | *Grams per liter.* | *Grams per liter.* | *Grams per liter.* | *Grams* (1a—2). | *Per cent.* |
| $SiO_2$ | 0.22 | 0.99 | 0.70 | 0.29 | 0.40 |
| Fe | .06 | .27 | .02 | .25 | .35 |
| Ca | 2.75 | 12.35 | 12.22 | .13 | .18 |
| Mg | .86 | 3.86 | 2.88 | .98 | .35 |
| Na | 15.85 | 71.17 | 45.88 | 25.29 | 34.95 |
| K | .51 | 2.29 | .35 | 1.94 | 2.68 |
| $HCO_3$ | .37 | 1.66 | .02 | 1.64 | 2.27 |
| Cl | 32.07 | 143.99 | 102.14 | 41.35 | 57.82 |
| | 52.69 | 236.60 | 164.21 | 72.37 | 100.00 |
| Ca+Cl | 0.086 | | 0.120 | | |
| Na+Cl | .494 | | .449 | | |

**Weights and proportions of compounds whose removal from 4.490 liters of water 1, together with evaporation, would yield 1 liter of water 2.**

[Recalculated from No. 3, above.]

| | Grams. | Per cent. |
|---|---|---|
| $SiO_2$ | 0.29 | 0.39 |
| $CO_2$ | .59 | .80 |
| $H_2O$[a] | .24 | .33 |
| $FeCO_3$ | .52 | .71 |
| $CaCO_3$ | .33 | .45 |
| $MgCO_3$ | .48 | .66 |
| $MgCl_2$ | 3.30 | 4.56 |
| NaCl | 62.92 | 86.98 |
| KCl | 3.70 | 5.12 |
| | 72.37 | 100.00 |

[a] This represents only the water from bicarbonates, a very small amount in comparison with the water lost by evaporation.

1. Brine from Berea sand; depth 1,748 to 1,760 feet; sample collected April 28, 1915, from a gas well 1½ years old situated in an old gas field at Summerfield, Marion Township, Noble County, Ohio. S. C. Dinsmore, analyst.

1a. Same water as No. 1 hypothetically concentrated to 22.37 per cent of its original volume (factor 4.490).

2. Brine from Big Injun sand; depth 1,200 feet; sample collected April 27, 1915, from a new gas well in an old gas field at Summerfield, Marion Township, Noble County, Ohio, 2½ miles from well in which sample 1 was obtained. S. C. Dinsmore, analyst.

3. Represents approximately the weights and relative proportions of the different constituents whose removal from 4.490 liters of water 1, together with evaporation, would yield 1 liter of water 2.

TABLE 22.—*Comparison of analyses of two oil and gas field waters from different geologic horizons, showing the constituents whose removal from the more dilute water, together with evaporation, would yield the more concentrated water.*

| | 1 | 1a | 2 | 3 | |
|---|---|---|---|---|---|
| | *Grams per liter.* | *Grams per liter.* | *Grams per liter.* | *Grams (1a—2).* | *Per cent.* |
| $SiO_2$ | 0.14 | 0.66 | 0.14 | 0.52 | 0.38 |
| Fe | .01 | .05 | .02 | .03 | .02 |
| Al | .50 | 2.35 | .62 | 1.73 | 1.26 |
| Ca | 2.79 | 13.11 | 12.98 | .13 | .09 |
| Mg | 1.01 | 4.75 | 1.69 | 3.06 | 2.22 |
| Na | 19.49 | 91.60 | 43.40 | 48.20 | 34.99 |
| K | .50 | 2.35 | 2.47 | .12 | |
| $CO_3$ | | | | | |
| $HCO_3$ | .05 | .24 | .04 | .20 | .15 |
| $SO_4$ | | | | | |
| Cl | 38.69 | 181.84 | 97.96 | 83.88 | 60.89 |
| | 63.18 | 296.95 | 159.32 | 137.63 | 100.00 |
| Ca÷Cl | 0.072 | | 0.133 | | |
| Na÷Cl | .503 | | .443 | | |

**Weights and proportion of compounds whose removal from 4.700 liters of water 1, together with evaporation, would yield 1 liter of water 2.**

[Recalculated from No. 3 above.]

| | Grams. | Per cent. |
|---|---|---|
| $SiO_2$ | 0.52 | 0.38 |
| $CO_2$ | .07 | .05 |
| $H_2O$[a] | .03 | .02 |
| $FeCO_3$ | .06 | .04 |
| $CaCO_3$ | .10 | .08 |
| $CaCl_2$ | .28 | .21 |
| $MgCl_2$ | 12.00 | 8.72 |
| NaCl | 124.69 | 90.50 |
| | 137.75 | 100.00 |

[a] This represents only the water from bicarbonates, a very small amount in comparison with the water lost by evaporation.

1. Brine April 30, 1915, from Berea sand; depth 1,570 to 1,592 feet; from an old oil and gas well in an old oil and gas field, Chaseville, Seneca Township, Noble County, Ohio. S. C. Dinsmore, analyst.

1a. Same water as No. 1, hypothetically concentrated to 21.28 per cent of its original volume (factor 4.700).

2. Brine from Keener sand; depth 870 to 880 feet; sample collected May 1, 1915, from an old oil and gas well in an old oil and gas field, Chaseville, Seneca Township, Noble County, Ohio, 1 mile from well in which sample 1 was obtained. S. C. Dinsmore, analyst.

3. Approximately the weights and relative proportions of the different constituents whose removal from 4.700 liters of water 1 would yield 1 liter of water 2.

TABLE 23.—*Comparison of analyses of two oil and gas field waters from different geologic horizons, showing the constituents whose removal from the more dilute water, together with evaporation, would yield the more concentrated water.*

| | 1 | 1a | 2 | 3 | |
|---|---|---|---|---|---|
| | *Grams per liter.* | *Grams per liter.* | *Grams per liter.* | *Grams* (1a—2). | *Per cent.* |
| $SiO_2$ | 0.24 | 0.37 | 0.12 | 0.25 | 0.67 |
| Fe | .01 | .01 | .05 | —.04 | .......... |
| Al | .49 | .76 | .83 | —.07 | .......... |
| Ca | 10.29 | 15.94 | 15.82 | .12 | .32 |
| Mg | 1.85 | 2.87 | 1.87 | 1.00 | 2.68 |
| Na | 33.76 | 52.30 | 40.79 | 11.51 | 30.80 |
| K | .26 | .40 | .95 | —.55 | .......... |
| $HCO_3$ | .02 | .03 | .03 | .......... | .......... |
| $SO_4$ | .12 | .19 | .13 | .06 | .16 |
| Cl | 78.78 | 122.04 | 97.61 | 24.43 | 65.37 |
| | 125.82 | 194.91 | 158.20 | 36.71 | 100.00 |
| Ca+Cl | 0.131 | .......... | 0.162 | .......... | .......... |
| Na+Cl | .429 | .......... | .418 | .......... | .......... |

**Weights and proportions of compounds whose removal from 1.549 liters of water 1, together with evaporation, would yield 1 liter of water 2.**

[Recalculated from No. 3 above.]

| | Grams. | Per cent. |
|---|---|---|
| $SiO_2$ | 0.25 | 0.67 |
| $CaCl_2$ | .26 | .70 |
| $MgCl_2$ | 3.92 | 10.48 |
| NaCl | 32.86 | 87.94 |
| $CaSO_4$ | .08 | .21 |
| | 37.37 | 100.00 |

1. Brine from Hundred-foot sand; depth 1,018 to 1,035; sample collected in September, 1915, from a new oil well in a new oil and gas field where production had not yet begun, Harlan Book farm, on Muddy Creek in Clay Township, Butler County, Pa., S. C. Dinsmore, analyst.

1a. Same water as No. 1, hypothetically concentrated to 64.55 per cent of its original volume (factor 1.549).

2. Brine from Bowlder sand; depth 1,701 to 1,720 feet; sample collected in September, 1915, from a new oil well in a new field where production had just begun, Welsh farm, Penn Township, Butler County, Pa., 12½ miles from field in which sample 1 was obtained. S. C. Dinsmore, analyst.

3. Approximately the weights and relative proportions of the constituents whose removal from 1.549 liters of water 1, together with evaporation, would yield 1 liter of water 2.

## EVIDENCE OF THE NATURAL ESCAPE OF GASES.

Examples of gases escaping from their reservoir rocks under such conditions as would probably bring about the concentration of associated waters are found to-day in many parts of the world, and it is doubtful if there are any important oil and gas regions where surface evidences of the escape of gases are absent. The common association of gas with oil and the almost invariable evidence of the natural escape of oil from the known deposits substantiate this statement.

At numerous places in the Appalachian fields gas escapes in shallow-water wells and in springs, such, for instance, as have given rise to the name Burning Springs, in Wirt County, W. Va. The gas springs in Wirt and Kanawha counties, W. Va., have been described in the county reports of the West Virginia State Geological Survey. Similar occurrences in western New York have been repeatedly described. Concerning the natural escape of gas near Fredonia, Chautauqua County, N. Y., Orton[1] says: "From some of these joints gas constantly escapes. The currents are much weaker, however, at the present time than they were in earlier days. When water occupies the openings formed by the joints, the gas appears in bubbles, forcing its way through the water. Such springs were known by the early French explorers of the country as "fontaines qui bouillent." Escaping gas is also reported in Jefferson[2] and Allegany[3] counties, N. Y. Campbell[4] reports the escape of natural gas from rock crevices near Richlands, Tazewell County, Va. Munn[5] reports gas seepages near Memphis, Tenn. Gas springs are reported in New Brunswick and Alberta, Canada, by Clapp and others.[6] Wegemann[7] reports a gas seepage in Palo Pinto County, Tex. "A bubbling spring of salt water," where gas is evidently escaping, has also been observed in the central Australian desert by Gregory.[8]

Probably the most striking examples of the natural escape of the hydrocarbon gases are afforded by the so-called mud volcanoes, which emit enormous volumes of combustible gas, together with concentrated brines, mud, and sand. Thompson[9] describes mud volcano phenomena in Russia, Borneo, Sumatra, Burma, Colombia, and Trinidad. He describes violent eruptions of gas, which becomes ignited, in the Poota and Bingadi districts, near Baku, Russia, and he also states that "on the ridge of hills fringing the Poota Valley near Baku there is an area of about an acre where the escaping gas is rarely if ever extinguished." "In the Yenangyat district of Burma a somewhat similar phenomenon is observed at Yenang Daung." The same writer describes many other outbursts of gas, some of them occurring under subterranean conditions.

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[1] Orton, Edward, Petroleum and natural gas in New York: New York State Mus. Bull., vol. 6, No. 30, p. 495, 1899.

[2] Idem, p. 457.

[3] Haworth, Erasmus, Report on oil and gas: Kansas Univ. Geol. Survey, vol. 9, p. 11, 1908.

[4] Campbell, M. R., personal communication.

[5] Munn, M. J., Explorations for natural gas and oil at Memphis, Tenn.: Resources of Tennessee, vol. 2, No. 2, pp. 48–50, 1912.

[6] Clapp, F. G., Petroleum and natural gas resources of Canada, vol. 2, pp. 52–53, 294–295, 1915.

[7] Wegemann, C. H., A reconnaissance in Palo Pinto County, Tex., with special reference to oil and gas: U. S. Geol. Survey Bull. 621, p. 53, 1916.

[8] Gregory, H. E., Lovely Australia, the unique continent: Nat. Geog. Mag., vol. 30, p. 556, 1916.

[9] Thompson, A. B., Oil-field development, pp. 176–184, New York and London, 1916.

Relative to the salt industry of the East Indies, Harris[1] says:

> On the Island of Java salt is also made from brine springs, which flow from Miocene beds and usually contain iodine and bromide salts, as well as sodium chloride. Many of these brines contain petroleum and gas. The most striking are those of Grobogan, northeast of the city of Samarang, in north-central Java. According to Karsten, the brines, which are associated with mud volcanoes, are in a limestone formation that forms a circular plain half a mile in extent. The brine springs occur in large numbers and boil from fissures in the rocks. The water is strongly saline and gives very good salt on evaporation. In the center of the limestone region is a remarkable volcanic phenomenon. On approaching this from a distance one sees a dense cloud of steam that at intervals of several seconds rises and then disappears. This is accompanied by a roar like distant thunder. Near by one perceives a hemispherical mass about 16 feet in diameter, composed of black mud saturated with salt water. This mass is regularly raised to a height of 30 feet by an underground force and then explodes with a deafening roar, and globular masses of the black mud are thrown in every direction. After an interval of two to four seconds the mass of mud is again raised and again torn to pieces by an explosion. For many years the natives have obtained salt by evaporating the brines ejected by these mud volcanoes. The salt water is led away in ditches to the outskirts of the region and is then evaporated. Some 200 metric tons are made annually.

In considering the subject further Harris adds that "small mud volcanoes with pools of salt water are also found on Ceram, one of the Spice Islands."

The escape of gases, especially methane, from unconsolidated carbonaceous sediments is so common as to require no particular comment.

Shaw[2] has described emanations of gases from the unconsolidated sediments at the mouths of Mississippi River. Knapp[3] describes gas seeps in Terrebonne Parish, La., and also quotes from the New Orleans Times-Democrat of November 26, 1911, an account of a gas eruption in the sea off Erin Point, Trinidad, on November 11, 1911. After describing the eruption, the account says: "The next day it was found that an island of 2½ acres had been formed. A landing party found the place still warm and by laying down boards were able to examine two cones, 12 to 15 feet high, from which gas was escaping. The air was saturated with the odor of sulphur and oil." In the same contribution Knapp quotes a report that gas is continually forcing up cones of pitch and mud in the pitch lakes region of Trinidad.

The occurrence of native bitumens filling fissures is in some localities a surface indication of the presence of oil and gas deposits in deeper reservoir rocks. In other fields fissures filled by calcite with scattered inclusions of waxy hydrocarbons are considered an indication of oil or gas. The solubility of certain waxy hydrocarbons in gases under high pressure and the relative insolubility of these hydrocarbons in the same gases under lower pressures, as well as the fact that much gas is evolved during the mining of native bitumens, suggest that vein deposits of these substances may owe their origin largely to the influence of gases that escaped through fissures. Thompson[1] states that masses of bitumen are often ejected with violence from the working faces of bitumen mines by gas which has collected under pressure in the minerals.

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[1] Harris, G. D., Rock salt, its origin, geological occurrences, and economic importance in the State of Louisiana: Louisiana Geol. Survey Bull. 7, pp. 198–199, 1908.

[2] Shaw, E. W., The mud lumps at the mouths of the Mississippi: U. S. Geol. Survey Prof. Paper 85, pp. 11–27, 1913.

[3] Knapp, I. N., discussion of paper by Roswell H. Johnson, The rôle and fate of the connate water in oil and gas sands: Am. Inst. Min. Eng. Trans., vol. 51, pp. 593–597, 1915.

Twenty years ago I. C. White[2] called attention to the association of deep-seated deposits of petroleum and natural gas with a fissure deposit of grahamite in Ritchie County, W. Va., and attributed the formation of the grahamite in part to the escape or exudation of petroleum accompanied by its oxidation. He furthermore cited the occurrence of coaly bituminous material, believed to be some of the hydrocarbon minerals originating from petroleum, at depths of more than 1,600 feet as evidence that outflows of petroleum occurred in the Cairo region of West Virginia "at the close of the lower Carboniferous epoch." It seems probable that natural gas would have accompanied such outflows of petroleum.

Subsurface movements of gas unaccompanied by surface emanations, though probably common at the present time, can not be detected. Furthermore, as most of the natural gas seeps that have been described in the literature were detected by ebullitions of gas through surface waters, it is obvious that numerous seeps where the gas passes directly into the air have never been detected.

### RELATIONS BETWEEN THE GEOLOGIC HISTORY OF CERTAIN RESERVOIR ROCKS AND THEIR INCLUDED WATERS.

In the Woodsfield and Summerfield quadrangles, in southeastern Ohio, the occurrence of relatively dilute waters in the deeply buried Berea sand, which is overlain several hundred feet higher by the Big lime, Keener, and Big Injun sands, containing more concentrated waters (see Tables 21 and 22), is interesting because it suggests a relation between the geologic history of these reservoir rocks and the concentration of their included waters, namely, that the more concentrated brines are now found in the strata where geologic conditions were at one time favorable for the escape of gas and the consequent evaporation of water.

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[1] Thompson, A. B., Oil-field development, p. 197, New York and London, 1916.

[2] Origin of grahamite: Geol. Soc. America Bull., vol. 10, pp. 277-284, 1898.

The Berea sand in the Woodsfield and Summerfield quadrangles is lenticular and is interbedded in thick deposits of shale. It overlies the unconformity at the base of the Mississippian series and is overlain by several hundred feet of relatively impermeable shale. In other words, the lenses of Berea sand from which water samples were collected and studied for this bulletin have remained deeply buried since the overlying shales were deposited.

The Big lime, Keener, and Big Injun sands, on the other hand, closely underlie the old erosion surface that marks the unconformity between the strata of Mississippian and Pennsylvanian age, and in parts of the two quadrangles the Big lime sand has evidently been removed by the pre-Pennsylvanian erosion. Where these formerly shallow rocks were not eroded they were covered only by a relatively thin series of limestone, shale, and sandstone that would have permitted the escape of at least a part of their gaseous content. We therefore infer that the brines in the Big lime, Keener, and Big Injun sands were concentrated largely by the evaporative effect of escaping gases during pre-Pennsylvanian erosion. The evaporation may have been assisted by arid climatic conditions. During these changes the waters in the lenses of Berea sand would have remained less subject to evaporation because the sand was protected by a thick cover of relatively impermeable shales.

So far we have found nothing to contradict the conclusion set forth above, it being improbable that this lenticular part of the Berea sand would constitute a channel for the deep migration of water entering the bed at its outcrop.

## HYPOTHESES CONCERNING THE ORIGIN OF THE OIL AND GAS FIELD WATERS.

### HYPOTHESES PREVIOUSLY SUGGESTED.

Before fully stating our hypothesis relative to the formation of the deep-seated oil and gas field brines we will discuss some of the suggestions offered by other investigators. As long ago as 1875 Hunt[1] concluded that certain deep-seated chloride waters from Ontario, which are characterized by their large content of calcium and magnesium chlorides, are long-buried bitterns derived from the evaporation of ancient sea water which was considerably richer in calcium chloride than the sea water of the present day. He supposed that part of the sodium in this water had been deposited as sodium chloride and that the sulphate had been removed as gypsum. This hypothesis involves widespread arid conditions and an ancient sea containing a high proportion of calcium chloride. Arid conditions exist in certain parts of the world at the present time and may have occurred during past geologic periods that would have left the bitterns somewhere near their present positions.

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[1] Hunt, T. S., Chemical and geological essays, p. 117, Boston, 1875.

Though the character of the ancient sea has been a subject of much discussion, it remains extremely hypothetical. Hunt's hypothesis regarding the excessive calcium chloride content of early ocean water has been supported by Lane[1] in several contributions. Daly,[2] on the other hand, postulates a limeless ocean of pre-Cambrian time, and in a later contribution[3] he outlines the probable changes in the salinity of the ocean.

We believe that the abundance of marine fossils in sediments that are either oil and gas bearing themselves or are interbedded with productive sands proves that conditions in the early seas where such sediments were deposited were suited to marine life that could not have existed in brines such as are now derived from oil and gas bearing sands. The changes by which the brines have been formed are therefore inferred by us to have taken place since the inclusion of the waters in sedimentary deposits.

In order to explain the abundance of calcium chloride in certain oil-field waters, Washburne[4] offers the hypothesis that ancient sea water, after being entrapped in the sediments, has been deprived of its sodium chloride by precipitation due to concentration of the water by the drying influence of ascending rock gases, such as nitrogen, carbon dioxide, and methane, but he drops this hypothesis, with mere mention, in favor of the hypothesis that such waters have received calcium and magnesium as well as sodium chlorides in emanations from deep-seated basic magmas. The part played by gases in the concentration of the brines is the principal subject of the present contribution, but the assumption that deep-seated basic rocks have been the source of the calcium and magnesium chlorides seems, on consideration, to have but little evidence in its favor. There is no reason to assume that the oil and gas bearing strata are underlain by basic igneous rocks, and the data from deep drilling in the Appalachian fields furnish no substantiating evidence. Even were the presence of the basic igneous rocks proved, it would be difficult to conceive how magmatic emanations entering the deeper sediments during early or recent geologic time could have so extensively permeated the thousands of feet of overlying sediments.

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[1] Lane, A. C., The chemical evolution of the ocean: Jour. Geology, vol. 14, pp. 221–225, 1906; Mine waters and their field assay: Geol. Soc. America Bull., vol. 19, pp. 501–512, 1908; Connate waters of the Atlantic coast [abstract]: Science, new ser., vol. 32, p. 190, 1910.

[2] Daly, R. A., The limeless ocean of pre-Cambrian time: Am. Jour. Sci., 4th ser., vol. 23, pp. 93–115, 1907.

[3] Daly, R. A., Some chemical conditions in the pre-Cambrian ocean: Cong. géol. internat., 11$^e$ sess., Stockholm, 1910, Compt. rend., pp. 503–509, 1912.

[4] Washburne, C. W., Chlorides in oil-field waters: Am. Inst. Min. Eng. Trans., vol. 48, pp. 687–693, 1914.

In a well at Findlay, Ohio,[1] pre-Cambrian granite or granite gneiss was found at a depth of 2,770 feet. This granite rock is overlain by sediments, principally quartzites, calcareous sandstones, and dolomitic limestones, with interbedded clays and shales, which contain oil, gas, and salt water. A natural bittern, called Blue Lick water,[2] that occurs in beds of St. Peter (Lower Ordovician) age, was here found 780 feet above the granitic rocks and apparently in no way related to "basic magmas" as postulated by Washburne.

To substantiate his hypothesis, Washburne states that, in general, the total salinity of these oil-field waters increases with depth. There are, however, numerous exceptions to this rule. In the Woodsfield and Summerfield quadrangles, Ohio, brines from lenticular portions of the Berea grit are less saline than waters occurring in the Maxton, Big lime, Keener, and Big Injun sands, several hundred feet higher in the geologic section. The lenses of Berea sand, from which the relatively dilute waters are derived, are overlain and underlain by several hundred feet of shale. Other examples of deep-seated chloride waters at higher horizons than comparatively fresh water are cited in the literature.[3]

Richardson[4] has recently called attention to the improbability that the deep-seated brines in the Appalachian oil and gas fields are connate waters and suggests that they may have been formed by the prolonged leaching of great masses of sedimentary beds by percolating ground waters and by the diffusion of sodium chloride dissolved from deeply buried salt beds. The retention of the waters in the sediments is attributed largely to the troughlike structure of the Appalachian geosyncline.

Under certain conditions these factors have been influential, but they do not in themselves adequately explain the formation of the brines. Ground waters of meteoric origin must have leached the sediments to some extent, and where salt beds have been in contact with water-bearing strata salt has undoubtedly been transferred by diffusion. It is improbable, however, that salt beds have occurred in proximity to all the sands of the Appalachian oil and gas fields in which concentrated waters are now found, and the distances through which the diffusion of salt has been effective can only be conjectured. Some additional factors to account for the concentration of the waters seem necessary. It must also be noted that the salts derived through the complete evaporation of brines occurring in very deep strata, those relatively near the salt beds in the Appalachian fields, generally contain smaller proportions of sodium chloride than the salts from brines occurring in shallow sands that are separated from salt beds by thousands of feet of comparatively impermeable shale. This makes it desirable to explain more fully the causes for the differences in the relative proportions of the dissolved constituents in the oil and gas field waters.

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[1] Condit, D. D., Deep wells at Findlay, Ohio: Am. Jour. Sci., 4th ser., vol. 36, p. 123, 1913.

[2] Condit, D. D., op. cit. Orton, Edward, Ohio Geol. Survey Rept., vol. 6, p. 298, 1888.

[3] Sanford, Samuel, Saline artesian waters of the Atlantic Coastal Plain: U. S. Geol. Survey Water-Supply Paper 258, pp. 75–86, 1911.

Stephenson, L. W., and Palmer, Chase, A deep well at Charleston, S. C.: U. S. Geol. Survey Prof. Paper 90, pp. 69–94, 1915.

Rogers, G. S., Chemical relations of oil-field waters in San Joaquin Valley, Cal.: U. S. Geol. Survey Bull. 653, p. 21, 1917.

Lane, A. C., discussion of "Chlorides in oil-field waters," by C W. Washburne: Am. Inst. Min. Eng. Trans., vol. 48, p. 693, 1914.

[4] Richardson, G. B., Note on Appalachian oil-field brines: Econ. Geology, vol. 12, pp. 37–41, 1917; Note on the diffusion of sodium chloride in Appalachian oil-field waters: Washington Acad. Sci. Jour., vol. 7, pp. 73–75, 1917.

## PRESENT HYPOTHESIS.

The deep-seated brines of the Appalachian oil and gas fields, as viewed by us, are only in part the derivatives of waters of sedimentation which were included when the sediments were deposited. The chlorine in the brines has been derived directly or indirectly from the waters of sedimentation, but practically all the other noteworthy constituents have been derived, at least in part, from other sources.

Extensive migration and the partial expulsion of the originally included waters have been caused by the consolidating processes to which the sediments have been subjected, more especially by compacting due to the increasing weight of subsequently deposited material. Cementation, heat, rock movements, and the incursion of petroleum and natural gas have also taken part in causing the migration and expulsion of the interstitial waters.

During periods of erosion ground waters of meteoric origin have from time to time entered the sedimentary rocks and have been retained and buried together with the waters of sedimentation or their derivatives. The final retention of the waters has been due to deep burial under relatively impermeable covers, to the sealing of the rock interstices, and to the basin-like structure of the Appalachian geosyncline.

Profound changes in the waters subsequent to their inclusion in the sediments have resulted from the mere solution of certain rock constituents such as chlorides, sulphates, carbonates, and silicates, from organo-chemical processes such as the reduction of sulphates during the decomposition of organic matter; from chemical reactions brought about through the mixing of waters having different properties of reaction, which is illustrated on pages 50 and 75; from reactions due to heat, as described on page 72; and from reactions between the dissolved constituents of the waters and the constituents of the rocks with which the waters have been in contact, as described on page 74.

The waters have also undergone deep-seated concentration. This concentration, which we believe to have been an important factor in many of the changes that the waters have undergone, was assisted in some places by heat and very generally by moving or expanding gases, which have carried off water as vapor. The concentration thus brought about has been accompanied by the loss from the waters of certain dissolved constituents, such as carbon dioxide, together with other gases, carbonates of iron, calcium, and magnesium, small amounts of sulphates of barium, strontium, and calcium, and also small amounts of silica as quartz or combined with other minor constituents. Under favorable conditions the concentration has proceeded to the extent of causing the separation of sodium chloride with minor proportions of calcium, magnesium, and potassium chlorides.

In the succeeding pages these deep-seated processes, which have, no doubt, been closely related and which have acted together, so that their combined effects are now to be observed in the oil and gas field brines, are considered in detail.

## HISTORY OF THE OIL AND GAS FIELD WATERS.

### INCLUSION AND MIGRATION OF WATERS OF SEDIMENTATION.

During periods of sedimentation vast quantities of sea water are included interstitially in marine sediments.[1] The water content[2] of muds such as those recently deposited along sea coasts range from 40 or 50 per cent to as much as 90 per cent by volume. In freshly deposited, unconsolidated sands the water content may vary from 15 or 20 per cent to more than 30 per cent of the volume. King[3] has shown that the interstitially included waters of sedimentation, or "connate waters,"[4] as they have been called by some investigators, have probably undergone extensive upward migration toward the regions of least pressure during the consolidation and induration of the sediments. The processes of compacting under increasingly great pressure, rearrangement of the mineral constituents of the sediments, and cementation due to the deposition of dissolved mineral matter from interstitial waters were, no doubt, contributive causes of this expulsion of water. It also seems probable that thermal migration, due in part to the expansion of interstitial gases,[1] and migration resulting from pressure accompanying rock movement[2] may have been factors worthy of consideration.

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[1] King, F. H., Principles and conditions of the movements of ground water: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 2, p. 77, 1898.

[2] King, F. H., idem. Shaw, E. W., discussion of paper by R. W. Johnson, The rôle and fate of the connate water in oil and gas sands: Am. Inst. Min. Eng. Trans., vol. 51, p. 597, 1915.

[3] King, F. H., op. cit., pp. 59–294.

[4] The Century Dictionary defines the word "connate" as follows: "Inborn, implanted at or existing from birth." The word was first used to designate interstitially included waters of sedimentation by A. C. Lane (Mine waters and their field assay: Geol. Soc. America Bull., vol. 19, pp. 501–512, 1908).

Relative to the migration of waters of sedimentation, King[1] says:

> In the case of extensive beds of clay deposits which have given rise to shales and rocks of that type, it is not improbable that the extremely large original pore space of 40 to 50 per cent in these sediments has been reduced to its present small proportions[3] through compression; but be this as it may, there must even then have been a ground-water movement measured by the actual reduction of pore space which has taken place, for the water of sedimentation must of necessity have been expelled before the reduction of volume could have occurred.

He also says:[4]

> The final or nearly complete consolidation of 50,000 square miles of sediment 1,000 feet deep, having a pore space of 33 per cent, filled with water, involves the actual transfer to a different region of the equivalent of a sheet of water 50,000 square miles in area and 300 feet deep, when there is still left within the mass a pore space of 3 per cent filled with water.

There can be little doubt, therefore, that very great volumes of water of deposition have passed through or along relatively porous beds of sand, and that under favorable conditions water originally included in deeper sediments has been retained and is now found in sandstone reservoirs. If this is true, it follows that waters in oil and gas bearing strata can not be "connate" in the strict sense of the word.

Lane[5] has called attention to the original differences between waters of sedimentation. Some were probably fresh water, others may have been brackish or even highly concentrated waters from inclosed basins, but the greatest sources of these waters were seas, which were probably less saline than those of present time.[6] During their migration through the sediments the waters of sedimentation of different types must have undergone more or less mixing, both with waters of sedimentation of other types and with various ground waters of meteoric origin. The oil and gas field waters are believed to be largely the derivatives of these mixtures.

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[1] King, F. H., op. cit., p. 84.

[2] Daly, M. R., The diastrophic theory: Am. Inst. Min. Eng. Trans., vol. 52, pp. 1137–1151, 1916.

[3] The average total porosity of shales may be considered about 13 per cent.

[4] King, F. H., op. cit., p. 83.

[5] Lane, A. C., Mine waters and their field assay: Geol. Soc. America Bull., vol. 19, pp. 501–512, 1908.

[6] Daly, R. A., Some chemical conditions in the pre-Cambrian ocean: Cong. géol. internat., 11e sess., Stockholm, 1910, Compt. rend., pp. 503–509, 1912.

## CHANGES IN THE WATERS OF SEDIMENTATION.

The chemical changes that waters of sedimentation undergo soon after they are included in the sediments on the ocean floor have been investigated by Murray and Irvine,[1] who show that sea water associated with the deposits at the sea bottom is often of a different chemical composition from the normal sea water overlying the deposit, and especially so in the deposits known as blue muds. The mud waters were collected from coastal as well as pelagic deposits and are shown by a series of analyses to contain only about 50 per cent as much sulphate as the normal ocean water. This difference is attributed to the reducing effects accompanying the process of decomposition of organic matter. The reduction of the sulphate is accompanied by the formation of carbonate, the proportion of carbonate in the mud waters being thereby increased. At the same time an unstable sulphide of iron is deposited in the muds, imparting to them their characteristically blue color. It has been proved that the reduction of the sulphates and the contemporary formation of carbonate and sulphide are due not merely to the presence of decomposing organic matter but to the action of microorganisms.[2] Rogers[3] has recently contributed a detailed discussion of the reduction of sulphates in oil-field waters and cites evidence that the sulphates are reduced directly by contact with the constituents of petroleum and natural gas, as well as by bacterial action.

Ammonia and hydrogen sulphide formed from decomposing organic matter have been repeatedly detected in deep ocean water and bottom muds, and the proportion of ammonium salts in the mud waters exceeds that in normal ocean water. It has been suggested that ammonium carbonate, reacting with interstitially included calcium and magnesium salts, precipitates calcium carbonate and some magnesium carbonate.[4] This precipitation may be increased, experimentally, by boiling the solution. Relative to the changes in mud waters, Daly discusses the results obtained by Murray and Irvine[5] as follows:

> In the mud water calcium sulphate is absent, magnesium sulphate is deficient when compared with average sea water, calcium carbonate is increased, and

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[1] Murray, John, and Irvine, Robert, On the chemical changes in the composition of sea-water: Roy. Soc. Edinburgh Trans., vol. 37, pp. 481–507, 1895.

[2] Meyer, Lother, Chemische Untersuchung der Thermen zu Landeck in der Grafschaft Glatz: Jour. prakt. Chemie, Band 91, pp. 5–6, 1864. Planchud, E., Recherches sur la formation des eaux sulfureuses naturelles: Compt. Rend., vol. 84, p. 235, 1877; Sur la réduction des sulfates par les sulfuraires, et sur la formation des sulfures métalliques, naturels: Idem, vol. 95, p. 1363, 1882. Étard, A., and Oliver, L., De la réduction des sulfates par les êtres vivants: Idem, vol. 95, p. 846, 1882.

[3] Rogers, G. S., Chemical relations of the oil-field waters in San Joaquin Valley, Cal.: U. S. Geol. Survey Bull. 653, 1917.

[4] Daly, R. A., The limeless ocean of pre-Cambrian time: Am. Jour. Sci., 4th ser., vol. 23, pp. 93–115, 1907.

[5] Murray, John, and Irvine, Robert, op. cit.

magnesium carbonate and ammonium sulphate are both present. The high chlorides show that the carbonates are not in excess because of fresh-water inflow. The ratio of magnesium carbonate to calcium carbonate is 1:3. When the clear water filtered from the mud was boiled for a short time, a crystalline precipitate was thrown down, consisting of 73.3 per cent calcium carbonate and 26.7 per cent magnesium carbonate. The formation of both carbonates is ascribed by Murray and Irvine to the reaction of ammonium carbonate chiefly on the sulphates, a conclusion which can not be doubted, especially in view of the presence of ammonium sulphate in the mud water. The alkaline carbonate was, of course, derived from decaying animal matter contained in the muds.

The slight increase in ~~the proportion of chlorine, due to its~~ retention while certain other constituents are ~~lost from~~ solution, ~~is another~~ step toward the formation of the brines.

To what extent the chemical changes continue during the deeper burial of the mud waters can only be conjectured, though it seems certain that the waters associated with buried organic matter must have been changed during the formation of natural gas and petroleum. We would therefore accept Rogers's conclusions that sulphates were practically removed from the waters during the earlier part of the period when they were buried or during their long association with organic matter. As ammonia and carbon dioxide are not found in any noteworthy concentration in the Appalachian oil-field waters, it seems logical to assume that those compounds have either escaped with other gases or entered into more stable combinations.

Another striking characteristic remaining to be explained is the calcium and magnesium content of these deep-seated waters. Possibly the common occurrence of dolomitic limestones in oil and gas bearing strata may throw some light on this problem. It seems probable that some of the magnesium in dolomite may have been contributed directly to the sediments by the same organisms that secreted calcium carbonate.[1] In addition to this, magnesium in solution may have been exchanged in part with the calcium in solid calcium carbonate, thus forming dolomite. Experimental evidence for and against this possibility is presented by Clarke.[2]

An essential requirement for the formation of dolomite by the last-mentioned reaction appears to be an appreciable elevation of temperature. But if a moderate elevation of temperature is postulated there is the simple possibility that during thermal concentration the solutions undergo hydrolysis and magnesium is precipitated as hydroxide, basic carbonate, or carbonate, as indicated by the studies of Davis[1] and Fisher.[2] The reactions, which for simplicity may be regarded as those accompanying the hydrolysis of a solution of magnesium carbonate or of magnesium chloride—

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[1] Clarke, F. W., and Wheeler, W. C., The inorganic constituents of marine invertebrates: U. S. Geol. Survey Prof. Paper 102, 1917.

[2] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, pp. 559–570, 1916.

$$MgCO_3+H_2O=Mg(OH)_2+CO_2$$
$$MgCl_2+2H_2O=Mg(OH)_2+2HCl$$

would be followed by the evolution of carbon dioxide, according to the first equation cited or from the reaction of the hydrochloric acid with carbonates.

If, for instance, a reaction according to the second equation should take place in the presence of calcium carbonate, calcium chloride, carbon dioxide, and water would be formed. A striking example of this was observed during the field studies relative to this bulletin. The water jackets of the gas engines used for pumping oil and water from the wells become badly caked with calcium carbonate crusts when shallow well waters are used for cooling the engines. To remove these crusts oil-well brines are passed through the water jackets. When subjected to the heat of the engines the magnesium chloride in solution in the brines hydrolyzes according to the second equation and the calcium carbonate crusts are removed as calcium chloride, carbon dioxide, and water according to the reaction

$$CaCO_3+2HCl=CaCl_2+CO_2+H_2O$$

The fact that these changes take place when the oil-field brines are subjected to moderate heat gives direct evidence bearing on the possible loss of magnesium and accession of calcium in the waters. It must also be observed that the introduction of calcium chloride into the deep-seated waters would affect the solubility of sodium chloride in the same solutions and thus influence the changes that have been noted. In the absence of recorded quantitative data on this subject we have determined the solubility of sodium chloride at 25° C. in the presence of different amounts of calcium chloride, with the results stated in Table 24. The solutions were agitated in a thermostat for a period of over two hours for each determination. The specific gravity was determined by weighing 5 or 10 cubic centimeter portions run out from a pipette after filling the pipette by suction through a small asbestos cap which served as a filter.

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[1] Davis, W. A., Studies of basic carbonates: Soc. Chem. Ind. Jour., vol. 25, p. 788, 1906.
[2] Fisher, Ferd, Dingler's Polyt. Jour., vol. 212, p. 208.

TABLE 24.—*Solubility of sodium chloride in water containing calcium chloride at 25° C.*

| Specific gravity of solution. | $CaCl_2$ in solution (per cent by weight). | NaCl in solution (per cent by weight). |
|---|---|---|
| 1.202 | 0.000 | 26.43 |
| 1.207 | 1.103 | 25.30 |
| 1.210 | 2.160 | 24.32 |
| 1.209 | 3.220 | 23.37 |
| 1.216 | 5.451 | 20.43 |
| 1.220 | 7.598 | 19.17 |
| 1.225 | 9.500 | 17.55 |
| 1.233 | 11.48 | 15.91 |
| 1.241 | 17.77 | 10.54 |
| 1.257 | 21.00 | 8.05 |
| 1.276 | 24.58 | 5.63 |

It will be observed from this table that the solubility of sodium chloride is greatly diminished by the presence of calcium chloride. This accords with the fact that the concentrated oil and gas field waters containing the greatest proportions of calcium chloride also contain the smallest proportions of sodium chloride.

Evidence in regard to the precipitation of magnesium from heated sea water is given by Rowan,[1] who presents a series of analyses of boiler crusts formed from sea water. These crusts contain from 1.8 to 40 per cent of magnesium oxide. The crusts containing the most magnesium and least calcium were deposited at relatively low temperature and pressure. Those containing the most calcium and the least magnesium were deposited at relatively high pressure and temperature. Magnesium was probably precipitated as hydroxide and calcium as calcium sulphate.

It is also very probable that magnesium has been lost from the waters to form magnesium silicates. Hunt[2] has proved that magnesium chloride reacts with calcium silicates to form magnesium silicates and calcium chloride. That this or a similar reaction may have caused the removal of magnesium and the introduction of calcium into the waters is made to appear more probable by the fact that secondary magnesium silicates (chlorites) are disseminated through some of the oil and gas bearing rocks.

In discussing the interaction between certain silicates and the dissolved constituents of saline waters Sullivan[3] refers to the early investigations of Lemberg, as follows:

> In 1870 Lemberg began the publication of his work on the transformation of silicates by salt solutions. His experiments, whose number runs into the hundreds, constitute a mine of important observations in the chemistry of minerals

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[1] Rowan, F. J., The practical physics of the steam boiler, p. 618 (appendix 8), New York, D. Van Nostrand & Co., 1903.

[2] Hunt, T. S., Chemical and geological essays, p. 122, 1878.

[3] Sullivan, E. C., The interaction between minerals and water solutions, with special reference to geologic phenomena: U. S. Geol. Survey Bull. 312, p. 20, 1907.

and of geologic processes. The silicates used were, in the main, those related to the zeolites, but others were included. The solutions were chiefly of salts of the alkalies and alkaline earths, but embraced also such bases as iron, aluminum, silver, and thallium. The outcome of the experiments was usually either (1) exchange of bases in equivalent quantity between silicate and solution; (2) addition of base to the silicate, especially from alkaline solution; (3) addition of entire salt; or (4) addition or subtraction of water. Frequently, if not usually, transformation to a different mineral species, often crystalline in form, ensued. Most of the work was done at temperatures ranging between 100° and 200° C., although some of it was performed at ordinary room temperature. The first papers[1] contain studies of the action of magnesium salt solutions on such silicates as apophyllite, gehlenite, vesuvianite, datolite, and wollastonite; practically equivalent substitution of magnesium for calcium and potassium took place. The work with wollastonite was conducted at room temperature and also at 100° C., with the following results:

*Action of magnesium sulphate on wollastonite.*

| | CaO. | MgO. |
|---|---|---|
| Wollastonite, original content | 44.1 | ........... |
| Wollastonite after contact with $MgSO_4$ solution: | | |
| Two years at room temperature | 27.4 | 11.5 |
| Twenty-five days at 100° C. | 1.0 | 32.0 |

The action is the same in the cold as at 100°—an approximately equivalent exchange of calcium for magnesium.

Palmer[2] has called our attention to the long-established use of sodium silicate as a precipitant of magnesium from hard waters containing both magnesium and calcium and suggests that similar reactions may have occurred in nature. Artificial zeolites (complex alkali aluminosilicates), under the name permutite, have recently come into use in water softening. Hard water filtering through a bed of this material deposits its calcium and magnesium and takes up an equivalent amount of sodium. The permutite is regenerated by passing through it a strong solution of sodium chloride, the magnesium and calcium in the bed being thereby carried out as magnesium chloride and calcium chloride, and the sodium zeolite is renewed. The reaction is reversible, going in one direction or the other in accordance with the concentration of calcium and magnesium or of sodium in the solution.

The type reaction between the constituents of a hard water and an alkali aluminosilicate may be expressed as

$$Na_2Al_2Si_2O_8+Ca(HCO_3)_2=CaAl_2Si_2O_8+2NaHCO_3$$

in which K may be substituted for Na; $SO_4$, 2Cl, or $2NO_3$ for

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[1] Deutsch. geol. Gesell. Zeitschr., vol. 22, pp. 335, 803, 1870; vol. 24, p. 187, 1872.

[2] Palmer, Chase, personal communication.

$2(HCO_3)$; and Mg, Ba, or Sr for Ca. The type reaction when the process is reversed may be expressed as

$$CaAl_2Si_2O_8+2NaCl=Na_2Al_2Si_2O_8+CaCl_2$$

in which Mg, Ba, or Sr may be substituted for Ca, and K for Na, as in the preceding reaction.

It appears probable that the hydrated alkali aluminosilicates which occur as disseminated constituents in shales and sandstones or in beds such as the bentonite deposits of the western United States, and which originated through the decomposition of igneous and metamorphic rocks, have caused changes in these deeply buried waters similar to those just described. For instance, it is possible that hard waters containing calcium and magnesium, reacting with certain hydrated alkali aluminosilicates in the reservoir rocks, or with the constituents of primary alkaline waters such as are represented in Table 14 (pp. 42–43), have deposited calcium and magnesium. The subsequent incursion of concentrated sodium chloride waters would then convert the calcium and magnesium into chlorides, the reaction being accompanied by an equivalent loss of sodium from solution. It is significant that there is a wide range of glassy rocks and minerals and their derivatives which, when hydrated, will react to remove magnesium and calcium from hard waters and which will give up the calcium and magnesium thus removed if treated with a concentrated solution of sodium chloride. Many of these minerals and their hydrated decomposition products have been recognized during studies of deep-sea deposits collected by the *Challenger* expedition.[1] Feldspars and micas are common constituents of some of the oil and gas bearing rocks, and the fact that more of the alkali-bearing silicates are not recognized in the sedimentary rocks of the Appalachian oil and gas fields may be due to the more or less complete alteration of these minerals to yield calcium and magnesium bearing silicates or other secondary minerals. More detailed studies of the Appalachian oil and gas field sediments and of the bentonite deposits and their associated waters in the western United States will doubtless throw light on this subject.

Another reaction between the saline waters and certain minerals in the sediments is described by Sullivan,[2] who has discussed at some length the removal of potassium from saline waters through the selective action of hydrated aluminosilicates such as those that occur in muds and shales. The affinity of potassium for these silicates is greater than that of sodium, and hence they retain potassium in preference to sodium.

The concentration of the interstitially included waters by the removal of water vapor in escaping gases and to a less extent by the hydration of minerals probably began soon after the waters were buried, and, in conjunction with chemical reaction, it has resulted in the loss of several constituents, among which may be mentioned calcium carbonate, calcium sulphate, and possibly some magnesium sulphate, where sulphates were present. Under favorable conditions the concentration was also followed by the deposition of sodium chloride with calcium and magnesium chlorides as impurities. The repeated deposition and re-solution of the salts, accompanied by the more ready deposition of sodium chloride and the retention or more ready re-solution of calcium and magnesium chlorides might also have influenced the composition of the waters.

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[1] *Challenger* Rept., Deep-sea deposits, p. 321, 1891.

[2] Sullivan, E. C., op. cit., p. 22.

It is evident that there is a wide range of possibilities whereby the acquisition or loss of the various constituents in oil and gas field waters can be explained.

### DEEP-SEATED WATERS AS AGENTS OF CEMENTATION.

Waters having primary alkalinity—that is, waters whose alkalinity is in part such as is due to the hydrolysis of sodium and potassium carbonates—have been recognized by Palmer[1] as characteristic silica carriers, but when waters possessing primary alkalinity react with solutions possessing secondary salinity—that is, salinity such as is due to calcium and magnesium chlorides or sulphates—their capacity to carry silica may be diminished so that quartz and other silicates will be deposited. Calcite, which is a common cementing material in sedimentary rocks, may also result from the mixing of solutions having different properties of reaction, as just described, or it may be deposited from deep-seated waters through the loss of carbon dioxide from solution, as explained on page 48. There can be no doubt that during the complex changes that have affected the reservoir rocks included waters having different properties of reaction have mingled and reacted with one another in such a manner as to deposit certain of their dissolved constituents, thus cementing the sediments.

The deposition of quartz, calcite, and other cementing material is no doubt facilitated by the concentration of the mixtures. Such a process of cementation, through the agency of deep-seated waters, we believe to have been an important factor in the retention of gas, oil, and water through vast periods of geologic time. The sediments themselves, more especially the colloidal matter of muds, have furnished an ample source of silica and alumina for cementation.

### RETENTION OF WATERS ASSOCIATED WITH GAS AND OIL.

As the result of consolidating processes which probably began in the sediments soon after deposition[2] and which were accompanied by partial expulsion and rearrangement of interstitially included fluids, there have been gradual changes from conditions of hydraulic migration to those approaching capillary equilibrium. The resistance to movements of water through increasingly fine water-filled interstices, due to friction, adhesion, viscosity, and capillary phenomena, has gradually become so great as to prevent the escape of deeply buried water, oil, and compressed gases whose expansive power is commonly referred to as "rock pressure." Deep-seated conditions approaching equilibrium have then prevailed through vast periods of time but have been interrupted by readjustments due to rock movements and to variations in depth produced by the deposition or erosion of sediments. Both fissuring accompanying rock movements and erosion have in places permitted the escape or movement of gas, oil, and water until the rock passages again became sealed. The same conditions under which gas, oil, and water have been retained under great pressure have, of course, assisted in preventing the entrance of water from neighboring regions.

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[1] Palmer, Chase, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, p. 22, 1911.

[2] Leith, C. K., and Mead, W. J., Metamorphic geology, p. 191, New York, 1915.

## EVAPORATION OF WATER AT DEPTH.

### VARIABLES INVOLVED.

In considering the evaporation of water at depth it may be well to discuss briefly some of the principles that govern evaporation both from the surface of the earth and from the deep-seated rocks. Various factors that assist evaporation at the earth's surface, such as heat, wind, and dryness of the atmosphere, are well known, and analogous factors may be supposed to have influenced evaporation beneath the surface. But underground conditions differ from surface conditions in several particulars. For example, the temperature may be higher than that at the surface, the pressure may be and generally is considerably higher than atmospheric pressure, and the movement of gases is in general immensely restricted compared to movements of the atmosphere. The possible range in temperature and pressure is much greater than the normal range at the surface. It may be stated, however, that no conclusions in the present discussion depend for their validity on the existence of temperature greater than 200° C. or pressure greater than 200 atmospheres.

The choice of the variables that may be said to govern evaporation depends somewhat on whether one has in mind merely the process of evaporation or the rate and amount of evaporation at some particular place. ①The movement of gas may aid in transferring water vapor from one region to another, just as a dry wind assists evaporation from the earth's surface, a certain volume of gas being no sooner saturated than it is replaced by a fresh volume of unsaturated gas. ②Furthermore, gases may take up moisture, if water is present, not only at the time of formation of the gases, but subsequently, during expansion, as the expansion of a gas affords unsaturated space into which water will pass as vapor until the space is saturated. But in the examples just mentioned an unsaturated condition of the gas is tacitly assumed. The more common phenomenon below the surface will be that of an equilibrium between water vapor and aqueous solutions, and the essential variables governing evaporation will then be those affecting this equilibrium in one way or another. These variables are 1 temperature, ② pressure, and ③ salt content of the solution.

The discussion of evaporation may be made more precise by the use of the term "vapor pressure," which may be described as follows: If at a definite temperature a liquid is admitted into a vacuum, some of the liquid will evaporate and the vapor so formed will attain a definite pressure. This definite pressure is called the vapor pressure of the liquid at the given temperature, and when once it is attained the space is said to be saturated with the vapor. For every liquid there is a definite relation between temperature and the vapor pressure of the liquid. The relation between the vapor pressure of pure water and the corresponding temperature is shown by the vapor pressure curve in figure 5 (p. 81). The vapor pressure of aqueous solutions decreases with increasing proportions of dissolved salts, but both for pure water and for solutions the vapor pressure increases with rising temperature. It follows, therefore, that a moderate rise of temperature would largely offset the influence of dissolved salts.

Although vapor pressures may be measured by starting with a vacuum, as illustrated above, the amount of vapor in a given space and the corresponding partial pressure of the vapor formed from a liquid will be practically the same, according to Dalton's law, whether or not another gas is present, provided only that the other gas is one which does not react chemically with the vapor. The concentration of water vapor in a given volume of saturated gas may therefore be considered as known if the temperature and salt content of the solution involved are known. In a water-saturated sand gas pressure may be considered merely as one of the variables determining the volume of the gaseous space.

Certain physical conditions are obviously required to render the effects of evaporation at depth permanent, and the principal requirement is the exclusion of surface waters. Furthermore, in order to account for noteworthy effects produced by deep-seated evaporation it is necessary to postulate either long-continued evaporation at moderate temperature due to the formation and escape of relatively large quantities of gas in association with small quantities of water, or else, possibly, more extensive evaporation in conjunction with the escape of less gas at a higher temperature.

## LIMITING MOISTURE CONTENT OF NATURAL GAS.

In our preliminary consideration of this problem we assumed that among the gases that are chemically inert with respect to water, natural gas would be no exception in permitting the evaporation of water. Subsequently the suggestion was made by one of our colleagues that water might not evaporate into natural gas containing the vapors of various oils as it does into air. However, we find a statement in the literature that Pittsburgh natural gas carries 0.7 per cent by volume of moisture, although the temperature is not stated.[1] To remove any possible doubt on the matter, very careful determinations were made of the amount of moisture that the illuminating gas used in Washington, D. C., is able to take up under ordinary conditions, with results entirely confirmatory of our anticipations. The gas used had the following composition by volume:

*Composition of illuminating gas used in Washington, D. C.*

| | | | |
|---|---|---|---|
| Carbon dioxide | 3.3 | Hydrogen | 33.5 |
| Oxygen | .6 | Methane | 15.0 |
| Benzol | .6 | Ethane | 1.2 |
| Toluol | .2 | Nitrogen | 3.5 |
| Xylol, etc | .4 | | |
| Ethylene | 10.9 | | 97.9 |
| Carbon monoxide | 28.7 | | |

A considerable volume of gas was passed into a large bottle over water, the bottle serving as a reservoir. For each determination a portion of the gas was passed from the bottle, first through a saturator to saturate the gas with moisture at a definite temperature, and then through weighed calcium chloride tubes to retain the moisture. The calcium chloride tubes were weighed again, and the increased moisture content was determined. The volume of gas used was calculated from the volume of water flowing out of an aspirator. The water in the aspirator had first been saturated with gas in order to prevent any interchange of gas between the water and the gas drawn in. The calcium chloride tubes were protected from a backward diffusion of moisture by a small additional calcium chloride tube. The pressure of gas in the aspirator and reservoir was kept equal to that of the atmosphere by regulating the flow of water or entrance of fresh gas. All temperatures were maintained as constant as possible, and the temperature of the saturator was measured by a thermometer giving a reading which was known to be correct within 0.02° C. on the hydrogen scale. The saturator consisted of a large U-tube containing strips of moist filter paper and enough water to seal the passage, the whole being immersed in a vessel of water which was maintained at a constant temperature. The calcium chloride tubes containing the moisture that had been removed by the gas were weighed with a counterpoise. The theoretical weights of water were calculated by equation (1) on page 81.

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[1] Burrell, G. A., and Robertson, I. W., The compressibility of natural gas at high temperatures: Bur. Mines Tech. Paper 131, p. 5, 1916.

The amounts of moisture found in the volumes of saturated gas used, together with the theoretical amounts that should be found, according to the gas laws, are shown in the following table. The results of some preliminary determinations are omitted because the temperature of saturation was not measured with sufficient accuracy to make them significant.

TABLE 25.—*Determination of moisture in saturated illuminating gas at Washington, D. C.*

| No. | Volume of gas used. | Temperature of saturator. | Weight of water found. | Weight of water calculated. |
|---|---|---|---|---|
| | *Cc.* | *°C.* | *Gram.* | *Gram.* |
| 1 | 2,001 | 22.29 | 0.0402 | 0.0395 |
| 2 | 1,990 | 20.93 | .0365 | .0363 |
| 3 | 1,986 | 20.85 | .0356 | .0361 |

From the results in Table 25 it is evident that the vapors of oily substances do not affect the evaporation of water into spaces occupied by natural gases. That a layer of oil on the surface of water might retard evaporation is admitted. But in the earth either there is abundant time for water to become distributed between the liquid and gaseous phases by diffusion under static conditions, or else gas, oil, and water occur so irregularly mixed as to bring them into new and frequent association during movement, as shown more fully on pages 25 and 95.

The weight of moisture in a given volume of saturated gas in contact with pure water depends, first of all, on the temperature, according to the well-known temperature-vapor pressure curve of water shown in figure 5. The vapor pressures for a number of temperatures, taken from the Smithsonian physical tables for 1916, are given in Table 26.

TABLE 26.—*Vapor pressure of water at different temperatures on hydrogen scale.*

| Temperature. | Pressure. | Temperature. | Pressure. | Temperature. | Pressure. |
|---|---|---|---|---|---|
| *°C.* | *Millimeters.* | *°C.* | *Millimeters.* | *C.°* | *Millimeters.* |
| 0 | 4.58 | 80 | 355.5 | 190 | 9,404 |
| 5 | 6.54 | 90 | 526 | 200 | 11,647 |
| 10 | 9.21 | 100 | 760 | 220 | 17,376 |
| 15 | 12.79 | 110 | 1,074 | 240 | 25,064 |
| 20 | 17.54 | 120 | 1,489 | 260 | 35,127 |
| 25 | 23.76 | 130 | 2,026 | 280 | 48,011 |
| 30 | 31.83 | 140 | 2,709 | 300 | 64,290 |
| 40 | 55.34 | 150 | 3,569 | 320 | 84,480 |
| 50 | 92.54 | 160 | 4,633 | 340 | 109,300 |
| 60 | 149.5 | 170 | 5,937 | 360 | 139,480 |
| 70 | 233.8 | 180 | 7,514 | 370 | 157,200 |

All quantitative deductions in this bulletin concerning the transportation of moisture by gases are based primarily on Table 26, which gives the vapor pressure when the gas is in contact with pure water. In dealing with a solution of salt instead of with pure water, it is necessary to apply a correction for the decrease of vapor pressure due to the dissolved substance. The vapor pressures of water from a great many kinds of solutions are known, so that almost any solution can be dealt with if required.[1] The relative lowering of the vapor pressure, $\frac{\Delta p}{p}$, where $p$ is the vapor pressure of water and $\Delta p$ is the lowering of vapor pressure due to the presence of a dissolved substance, is roughly independent of the temperature—a fact which simplifies the correction considerably. For instance, an 8 per cent solution of calcium chloride has a vapor pressure about 5 per cent lower than that of pure water, and a brine saturated with ordinary salt has a vapor pressure about 25 per cent less than that of pure water.

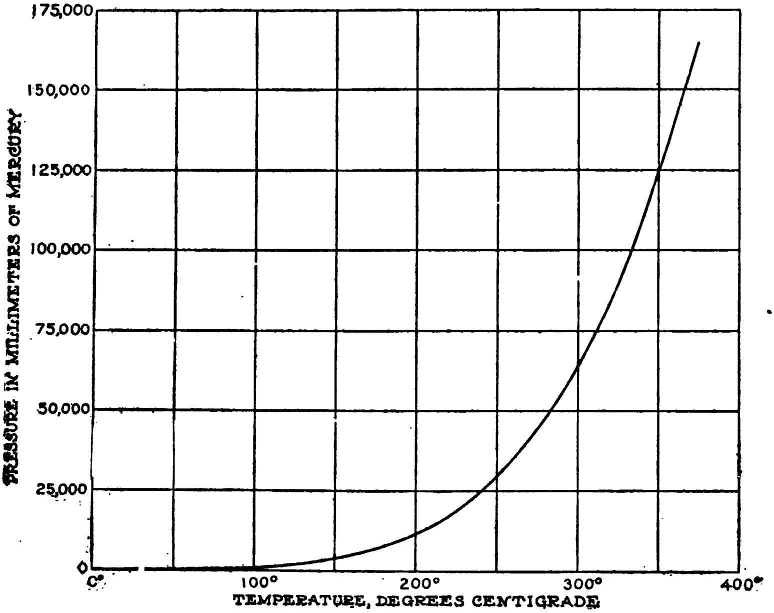

FIGURE 5.—Temperature-vapor pressure curve of pure water.

The amount of moisture in a given volume of saturated gas at a given temperature is computed from the vapor pressure at that temperature by the gas laws as follows:

$$w = \frac{Mpv}{RT} \tag{1}$$

where $w$ is the weight of the gas under consideration, in this case water vapor; $M$ its molecular weight, equal to 18 for water; $p$ the partial pressure of the particular gas, here the vapor pressure of water, measured in millimeters of mercury; $v$ the volume, in cubic centimeters, of the total space in which the gas is contained; $R$ the gas constant equal to 62,360; and $T$ the absolute temperature.

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[1] See any collection of physico-chemical tables, such as the Smithsonian physical tables or those of Landolt-Börnstein-Meyerhoffer.

In Table 27 will be found the weights of moisture for a number of temperatures computed by equation (1) and expressed in grams per cubic meter and in pounds per 1,000 cubic feet of gas. The pressures are stated in order to show the conditions necessary for the maintenance of the liquid phase. If the pressure at any given temperature were not equal to or greater than that stated in the table the water would completely evaporate and the weight of moisture would be smaller than that given in the table.

Without doubt there is considerable uncertainty in the weights calculated for the highest temperatures on account of deviations from the gas laws at the high pressures considered. Steam tables cover a part of the field and show slightly higher weights of steam at the higher temperatures and pressures. It is to be expected that as the density of a gas increases—owing, for instance, to compression—the molecules will be brought so much more closely together that they will exert an attraction for one another and cause deviations from the gas laws. The solubility of water vapor in compressed gases is therefore probably greater than that calculated in the tables, but experimental data on this point are lacking. For these reasons the calculated figures are retained only as first approximations. It can be seen from the tables that a given volume of gas can transport surprisingly large quantities of moisture at the higher temperatures.

TABLE 27.—*Weights of water in saturated gas.*

| Temperature (°C). | Pressure (atmospheres). | Weight of water. | |
|---|---|---|---|
| | | Grams per cubic meter. | Pounds per 1,000 cubic feet. |
| 0 | 0.006 | 4.84 | 0.302 |
| 10 | .012 | 9.39 | .586 |
| 20 | .023 | 17.27 | 1.078 |
| 25 | .031 | 23.01 | 1.436 |
| 30 | .042 | 30.32 | 1.893 |
| 40 | .073 | 51.02 | 3.185 |
| 50 | .122 | 82.69 | 5.163 |
| 60 | .197 | 129.5 | 8.085 |
| 70 | .308 | 196.7 | 12.28 |
| 80 | .468 | 290.6 | 18.14 |
| 90 | .692 | 418.1 | 26.10 |
| 100 | 1.00 | 510.7 | 31.88 |
| 110 | 1.41 | 809.9 | 50.57 |
| 120 | 1.96 | 1,093 | 68.24 |
| 130 | 2.67 | 1,451 | 90.60 |
| 140 | 3.56 | 1,893 | 118.1 |
| 150 | 4.70 | 2,435 | 152.0 |
| 160 | 6.10 | 3,088 | 192.8 |
| 170 | 7.81 | 3,866 | 241.3 |
| 180 | 9.89 | 4,788 | 298.9 |
| 190 | 12.37 | 5,861 | 365.9 |
| 200 | 15.32 | 7,107 | 443.7 |
| 220 | 22.86 | 10,170 | 635.0 |
| 240 | 32.97 | 14,090 | 879.7 |
| 260 | 46.22 | 19,020 | 1,187 |
| 280 | 63.17 | 25,060 | 1,564 |
| 300 | 84.59 | 32,370 | 2,021 |
| 320 | 111.10 | 41,110 | 2,566 |
| 340 | 143.80 | 51,450 | 3,212 |
| 360 | 183.50 | 63,600 | 3,971 |
| 370 | 206.80 | 70,550 | 4,405 |

## EFFECT OF THE INCREASE OF TEMPERATURE WITH INCREASING DEPTH.

As the temperature of the earth increases about 1° C. for every 100 feet of depth from the surface, it is evident that at depths of about 10,000 feet aqueous solutions would attain a temperature at which they would boil if under atmospheric pressure. But as the pressures prevailing underground tend to be greater than atmospheric pressure, the boiling points are likewise higher, so that it becomes somewhat problematic whether under ordinary conditions aqueous solutions would ever boil merely on account of the increase of temperature with increasing depth. If free egress for the vapor were blocked the conversion of much water into vapor would be prevented by the high pressure that would be produced. In fact, the pressure caused simply by the weight of a continuous column of water from any point in the earth to the surface would be great enough to prevent ebullition caused merely by the increase of temperature with depth. In deep unproductive wells filled with water, therefore, or in fissures and channels filled with water where the evolution of gas is not violent enough to displace the water, the boiling points would not be attained under the existing pressures.

As a matter of fact, however, a continuous column of water is not to be expected under the geologic conditions that prevail in most oil and gas fields. Strata such as the shales in which the more or less lenticular bodies of productive sandstone are interbedded are relatively impermeable, the water-filled rock interstices being sufficiently fine to modify the cumulative pressure effect of water in overlying beds. Moreover, the rock pores in some beds are filled with gas and oil, which would interfere with a so-called continuous water column. We see no reason to suppose, therefore, that pressures exactly equal to the hydrostatic pressures of corresponding water columns would be exerted upon gases at all depths down to the zone of rock flowage, although, as pointed out on page 28, the so-called rock pressure in many wells is roughly proportional to the depth. Observations in different oil and gas fields indicate that in relatively shallow rocks the gas pressure may be greater or less than would be caused merely by the hydrostatic head of a column of water reaching the surface.

It appears that at depths greater than about 10,000 feet the ebullition of aqueous solutions would be possible only under very favorable conditions, but if it occurred it would result in a great concentration of the solutions. Under the conditions that generally exist, however, there would be merely a high concentration of water in the vapor phase, and the removal of this water would await an escape of gas, which at the temperatures under consideration would result in a considerable transfer of moisture, leaving either salt or more concentrated solutions behind.

Dismissing the possibility of ebullition as being too slight to be of any great importance to the subject in hand, we feel certain that wherever there is a gas in the earth in contact with a liquid the concentration of vapor in the gas will be greater the greater the depth, owing to the increase of temperature with increasing depth.

### EFFECTS DUE TO CHANGES OF PRESSURE.

When a gas that is not saturated with water vapor is made to move through water or across a surface of water, it is evident that fresh volumes of gas are continually coming into contact with the water. No sooner does a certain part of the gas become saturated or partly saturated with water vapor than it is replaced by another lot of unsaturated gas, and in this way evaporation is hastened. At any given temperature the amount of water vapor required to saturate a certain volume of gas—that is, the amount of water vapor that can be evaporated into the fixed volume of gas—is the same whether the gas is blown through or across the water or whether the water and gas are at rest. The presence of the gas does not influence the total capacity of a given space to hold moisture but may afford the unsaturated space into which evaporation takes place. For instance, when a gas expands under a decrease of pressure, at a constant temperature, its capacity for taking up moisture is increased because the unsaturated space occupied by the gas in increased. An expanding gas must transport increasing amounts of moisture as long as its expansion continues at a constant temperature in the presence of water.

As already stated, we have no data as to how strictly the proportionality between volume and water content holds for very highly compressed gases, but proportionality can certainly be assumed over a wide range of pressures from low pressures up. Evaporation of water caused by an expanding gas can therefore be offered as an explanation of the concentration of the brines even when the original compressed gas is saturated with moisture, as the capacity of the gas for moisture is created entirely by the expansion.

If the simple proportionality just mentioned is assumed, a tenfold expansion of methane, for example, would create a tenfold space for moisture. In this way it may be calculated that a cubic meter of gas confined at a pressure of 100 atmospheres would be able to evaporate 5,049 grams of water by the time it had expanded to atmospheric pressure, if the expansion were gradual and in contact with pure water at 40° C. In contact with a saturated sodium chloride brine the loss by evaporation would amount to about 3,800 grams of water, which would cause the precipitation of about 1,400 grams of salt. The effects with other salts and other temperatures would differ, as has been previously stated.

The preceding figures apply to a temperature of 40° C. At other temperatures the results would be different. They would be different, also, if the expansion took place in such a manner as to involve a considerable fall in temperature. As a given volume of water-saturated gas passing under constant pressure from a warmer to a colder zone would deposit water, it is evident that pressure and ~~temperature must~~ be ~~considered conjointly~~. It is not difficult, however, to calculate by the gas laws what volume a gas would attain under any given temperature and pressure if its volume at any other temperature and pressure is known. The initial and final water content of the gas can therefore be obtained from Table 27, and the difference between these quantities will represent the weight of water that the gas would gain or lose, as the case may be. The principal difficulties are met in attempting to postulate conditions at considerable depths in the earth. A horizontal flow ~~of gas, very gradually~~ expanding in the presence of water, would certainly cause evaporation, for no effective change in temperature would be involved. For a vertical flow consideration must be given to the earth temperature gradient, and it is possible, ~~as already stated~~, that under certain conditions a decrease in temperature might overcome the evaporative effect of gas expansion. From the slope of the vapor-pressed curve it is evident that temperature is more likely to become the major variable at the higher temperatures.

Adiabatic expansion cools a gas, and when this effect is localized the cooling may be very considerable. For the purposes of our investigation, however, any condensation of moisture due to this cause in gas conduits may be considered an after effect. There may possibly be regional cooling in the earth as a result of such expansion, but the chances seem to us to lie rather in the other direction, which means that ascending gases will contribute heat to the inclosing rocks. However that may be, the volume and heat capacity of the strata are so great with reference to the probable quantities of gas involved that it seems logical to suppose that only small geologic temperature effects could be permanently produced in this way. We have therefore restricted our discussion to the temperature changes due to a normal earth gradient.

The belief that great amounts of the natural gases undoubtedly exist in the earth dissolved in water and oil is warranted by the known solubilities of gases in both water and oil and by the commonly observed escape of gases from these liquids during periods of production in oil and gas fields. An increase in pressure tends to increase the solubility of a gas in a liquid, and it follows that any decrease in pressure facilitates the concomitant liberation and expansion of a gas so dissolved. ~~Gases such as propane (below 97° C.) and some~~ other hydrocarbons, as well as hydrogen sulphide (below 100° C.),

~~may occur at considerable depth as fluids liquefied by pressure.~~ These fluids will of course vaporize and expand on release of the pressure, thus furnishing space into which water may also vaporize.

## SOLUBILITY OF NATURAL GAS IN OIL AND WATER.

Knowledge of the solubility of the hydrocarbons in oil under various conditions is meager. It is stated[1] that 1 volume of certain California oils absorbs 0.15 volume of the natural gas used in Pittsburgh, Pa., and that 1 volume of claroline oil dissolves 0.31 volume of pure methane and 1.96 volumes of pure ethane at atmospheric pressure. At higher pressure the amounts dissolved would be greater. These figures suggest that propane and higher hydrocarbons would be much more soluble than ethane. Nitrogen and oxygen are far more soluble in petroleum than in water, and ethylene is soluble to the extent of 0.14 volume in 1 volume of petroleum.[2] Other data on the solubility of certain hydrocarbons are given by McDaniel.[3]

The following table is quoted from Rogers:[4]

*Solubility of certain gaseous hydrocarbons in water.*

[At 20° C. and 760 millimeters pressure, except propane, which is at 17.8° C. and 753 millimeters pressure.]

| Name. | Formula. | Volumes soluble in 100 volumes of water. | Authority. |
|---|---|---|---|
| Methane | $CH_4$ | 3.31 | Winkler.[a] |
| Ethane | $C_2H_6$ | 4.72 | Do. |
| Propane | $C_3H_8$ | 6.50 | Lebeau.[b] |
| Butane | $C_4H_{10}$ | 0 | Frankland.[c] |
| Ethylene | $C_2H_4$ | 12.2 | Winkler.[d] |
| Propylene | $C_3H_6$ | 22.1 | Von Than.[e] |

[a] Winkler, L. W., Die Löslichkeit der Gasse in Wasser: Deutsche chem. Gesell. Ber., Band 34, pp. 1417-1421, 1901.

[b] Lebeau, Paul, Sur quelques propriétés physiques du propane: Compt. Rend., vol. 140, pp. 1454-1456, 1905.

[c] Frankland, Edward, Ueber die Isolirung der organischen Radicale: Annalen der Chemie, Band 71, p. 171, 1849. (Frankland states that butane is insoluble in water, but it is desirable that this early work be checked with the more refined methods now in use.)

[d] Winkler, L. W., unpublished data cited by Landolt-Börnstein, Physikalisch-chemische Tabellen, p. 604, 1905.

[e] Von Than, Carl, Der Absorptionscoefficient des Propylengases: Annalen der Chemie, Band 123, p. 187, 1862.

In general, as the density of a gas is increased, owing to compression, for instance, the molecules are brought so much more closely together that they begin to show some of the properties of liquids. It has been shown, for example, that methane at a pressure of 300 atmospheres acquires an appreciable solvent action on paraffine, which is deposited in brilliant spangles when the gas is allowed to expand to ordinary pressure.[1] Compressed ethylene is a still more active solvent of the higher hydrocarbons. So far as we can judge from the experimental evidence available, therefore, the behavior of water and of hydrocarbons toward gases shows a marked contrast. The expansion of a gas would tend to increase the evaporation of water, if present, but to cause the deposition of such higher hydrocarbons as might exist in the compressed gas.

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[1] Burrell, G. A., Seibert, F. M., and Oberfell, G. G., The condensation of gasoline from natural gas: Bur. Mines Bull. 88, pp. 29-34, 1915.

[2] Gniewosz, St., and Walfisz, A., Ueber die Absorption von Gasen durch Petroleum: Zeitschr. physikal. Chemie, vol. 1, p. 70, 1887.

[3] McDaniel, A. S., The absorption of hydrocarbon gases by nonaqueous liquids: Jour. Phys. Chemistry, vol. 15, pp. 587-610, 1911.

[4] Rogers, G. S., Chemical relations of the oil-field waters in San Joaquin Valley, Cal.: U. S. Geol. Survey Bull. 653, p. 106, 1917.

## ORIGIN OF THE GASES AS RELATED TO THE EVAPORATION OF THE ASSOCIATED WATERS.

To attempt to discuss in this bulletin the numerous theories relative to the origin of natural gas would be unwise. It is sufficient to state that, if classified according to their origin, two general types of deep-seated gases must be considered—those from deep-seated inorganic sources and those evidently formed from organic remains through the agency of microorganisms, heat, or chemical changes due to other causes. There is so little evidence to substantiate the hypothesis that the natural gases associated with petroleum are of inorganic origin that we give the subject only brief consideration. If inorganic gases entered the sediments the evaporative effects may have been similar, in some respects, to those of the organic gases. There is, however, some uncertainty as to the amount of moisture that would have been introduced into the sediments with gas of inorganic origin. The chemical effects upon oil and gas field waters that might accompany the incursion of such gases have been considered by Washburne.[2]

The gases of the second type, those formed in sediments through the agency of heat or chemical changes due to other causes, constitute a series of hydrocarbon gases whose principal constituents are methane and ethane, together with small amounts of hydrogen, hydrogen sulphide, carbon dioxide, and nitrogen. The formation and escape of enormous volumes of these natural gases in the presence of interstitially included waters would doubtless cause the evaporation and concentration of the waters from the very beginning of their burial. In discussing the probable changes in waters of sedimentation we have shown the possibilities for evaporation of this sort to occur. No doubt such evaporation has been a factor in bringing about the concentration of the waters under scrutiny.

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[1] Villard, P., Dissolution des liquides et des solides dans les gaz: Jour. physique, 3d ser., vol. 5, p. 453, 1896.

[2] Washburne, C. W., Chlorides in oil-field waters: Am. Inst. Min. Eng. Trans., vol. 48, pp. 687-693, 1914.

It is a familiar fact that in carbonaceous matter both the capacity to emit gases and the percentage of water present show a continuous decrease in the series from peat to anthracite. Porter and Ovitz[1] have shown that upon being allowed to stand at atmospheric pressure and ordinary temperature for five months after mining, a sample of bituminous coal yielded a volume of methane equal to one and three-fourths times the volume of the coal itself. Had the sample been subjected to heat or had it stood indefinitely a much greater volume of gas would probably have been emitted. Concerning the primary decomposition of coal by heat Taylor and Porter[2] say:

> A high-grade bituminous coal of the gas-making type decomposes by heat primarily into paraffine hydrocarbons and a completely altered nonvolatile residue, with small quantities of water, $CO_2$, and CO. The three latter products are the first produced, although in small quantity; from some other types of bituminous coal they are produced in greater relative quantities than from the gas-coal type. Complex and varied secondary reactions induced by superheating the hydrocarbons, water vapor, and $CO_2$ are of great importance in industrial high-temperature carbonization.
>
> The products of low-temperature carbonization from coal of the Pittsburgh type on an industrial scale at about 800° to 900° F. (427° to 482° C.) will consist of a rich gas amounting to 0.6 to 0.7 cubic foot per pound of coal, and a large yield of oil or tar, comprising 10 to 12 per cent of the coal. This tar consists chiefly of paraffin hydrocarbons, is very low or possibly entirely devoid of benzene and naphthalene derivatives, and practically devoid of free carbon. The gas will contain 6 to 7 per cent of unsaturated hydrocarbons and 20 to 25 per cent of ethane and its higher homologues and consequently will have a high calorific and illuminating value. The tar may be either redistilled or subject to cracking processes so as to produce light oils—gasoline substitutes—whose yield will be greater than and probably at least double that obtained by high-temperature carbonization.

The gas formed in such processes would of course take up moisture if water were present. Taking rough averages of various determinations, we have the following percentages of moisture in carbonaceous matter: Peat, 25 per cent; lignite, 20 per cent; bituminous coal, 8 per cent; anthracite, 1.6 per cent; and finally a graphitoid rock is recorded with only 1 per cent of moisture. The conclusion seems inevitable that gases escaped during the changes that converted peat into anthracite and that the escaping gases assisted in carrying off the water as water vapor. It also seems evident that gases have escaped and that water has been removed during the metamorphism of organic matter such as occurs in the carbonaceous shales frequently associated with oil and gas deposits.

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[1] Porter, H C., and Ovitz, F. K., The escape of gas from coal: Bur. Mines Tech. Paper 2, 1911.

[2] Taylor, G. B., and Porter, H. C., The primary volatile products of the carbonization of coal: Mines Tech. Paper 140, pp. 50–51, 1916.

## RELATED PHENOMENA AND DEDUCTIONS OF PRACTICAL VALUE.

### ASSOCIATION OF ROCK SALT WITH DEPOSITS OF NATURAL GAS AND PETROLEUM.

It is a matter of common knowledge that masses of rock salt are in many places associated with deposits of petroleum and natural gas. Striking examples are furnished by the salt domes of Louisiana and Texas, and somewhat similar occurrences of salt are reported in southern Vera Cruz, Mexico; in Algeria; in Hanover, Germany; and at Maros-Ujvas, Transylvania. Harris[1] gives a comprehensive summary of the rock-salt deposits in different parts of the world, showing that many of the salt masses in foreign countries resemble those of the Louisiana and Texas salt domes, both as to their general aspects and as to their probable mode of origin. Thompson[2] suggests that some of the structural features in Egypt, in the Hanoverian fields of Germany, and in the Ural-Caspian area may be due to salt-dome phenomena. He adds that it is not improbable that some of the structural features of the Rumanian and Galician oil fields are also associated with crystalline growths of salt that now form the "cores" of some of the oil fields.

Although these associations have puzzled many investigators, the facts that have been brought out in the present paper concerning the evaporative action of gases seem to establish the theory that natural gases under certain favorable conditions are able to concentrate natural waters, even to the point of depositing water-soluble salts. It is interesting in this connection to recall that Bunsen proved that the rock salt of Wielieczka contains marsh gas.[3] It is also interesting to note that in September, 1664, the first recorded explosion of fire damp occurred in the Hallstatt salt mine.[4] Marsh gas and hydrogen sulphide are both present in the salt masses of northern Germany and Galicia, and there are numerous records of inflammable gases in salt mines. Knapp[5] has recently described the exudation of both gas and oil under high pressure from the salt masses at Belle Isle, La. It would, however, be rash to deny that the salt beds now found near deposits of petroleum and natural gas in some parts of the world owe their development as well as their preservation to solar evaporation and to arid climatic conditions. We therefore differentiate between the two types of salt deposits and confine this discussion to those formed through deep-seated agencies.

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[1] Harris, G. D., Rock salt, its origin, geological occurrences, and economic importance in the State of Louisiana: Louisiana Geol. Survey Bull. 7, 1908; Oil and gas in Louisiana, with a brief summary of their occurrences in adjacent States: U. S. Geol. Survey Bull. 429, 1910.

[2] Thompson, A. B., Oil-field development, pp. 241–245, New York and London, 1916.

[3] Annales chimie et phys., 3d ser., vol. 38, p. 269, 1853.

[4] Harris, G. D., Rock salt, its origin, geological occurrences, and economic importance in the State of Louisiana; Louisiana Geol. Survey Bull. 7, p. 173, 1908.

[5] Knapp, I. N., discussion of paper by A. F. Lucas (A review of the exploration at Belle Isle, La.): Am. Inst. Min. Eng. Bull. 133, p. 88, January, 1918.

It is obvious that the evaporative effects due to moving gases will depend somewhat on the distribution ~~of water.~~ ~~Relatively small~~ amounts ~~of water subjected to evaporation into escaping gases would~~ be more readily concentrated so as to deposit salt than would excessive amounts of water. For instance, where the conditions are such as to permit the continued influx of surface waters, as in certain shallow strata of the Appalachian fields, the brines do not attain, or at least do not retain, the same degree of concentration as those in the deeper strata. If, on the other hand, small quantities of salt water trickling into a fissure should come into contact with unsaturated gases rising from some deeper source, the salt water would be evaporated and salt deposited in the fissure if the solution were sufficiently concentrated. The extreme concentration of some of the brines ejected from mud volcanoes has already been mentioned as being due partly to the removal of water by escaping gases.

It is not necessary that the gases escape to the surface in order to cause evaporation, for in deep-seated strata, under certain conditions, especially where the beds have undergone fissuring, gas may flow ~~from one bed where the pressure is high to another bed where~~ a ~~lower pressure prevails~~. ~~The evaporative effects of the migrating~~ gas would, under these conditions, be none the less important. The deposition of constituents other than chlorides, such as carbonates or sulphates, if they are present, might be caused by evaporation, so as to produce the unusual relations ~~sometimes~~ observed in salt domes. It also seems probable that where the salt masses are associated with deposits of calcium sulphate and calcium carbonate, geochemical processes yielding sodium chloride, together with the other compounds, have been brought about through the mixing of solutions that have different properties of reaction or through reactions between the constituents of certain solutions and those of the containing rocks.

## ORIGIN OF SALT DOMES.

It is our belief that salt domes, such as are found in Louisiana and Texas and seem to be closely related to the occurrence of natural gas and petroleum, have been formed in part by these geochemical processes accompanied by the evaporation of saline waters through the agency of escaping gases. Many of the domes occur along faults, and some of the salt masses are situated at the intersections of fault planes. It is also significant that emanations of the gaseous hydrocarbons are commonly associated with the salt domes.

The extensive literature dealing with the origin of salt deposits has been summarized by Hahn.[1] Harris [2] reviews in detail several of the theories that have been advanced to explain the origin of the salt domes in the Gulf region of the United States.

As early as 1901 Hill [3] wrote: "These uplifts are most probably due to isostatic movements rather than to accumulations of gas." The next year, however, he ventured the opinion that the domes were caused by the uplifting force of water or oil rising under enormous hydrostatic pressure.[4] In 1904 Hager [5] proposed the "volcanic plug" hypothesis, an important element of which is the view that the cause of the domes goes back to faulting and igneous activity in the deeper rocks, including the intrusion of laccoliths. Certain features of Hager's hypothesis seem to fit the later phases of the dome building so well that the following quotation is made from his article, though we do not consider igneous activity essential to the phenomena under discussion:

> By contact with the molten intrusives vast quantities of gas were generated from the reduction of metallic sulphides and the distillation of lignites and organic substances. These gases, accompanied by steam under tremendous pressure, forced their way to the surface through the unconsolidated sands and clays of the overlying Tertiary material, perhaps giving rise to mud volcanoes, such as occur in many of the world's great oil fields of the present day. Heated waters from great depths found vent along the same channels, carrying in solution carbonates of lime and magnesium, gypsum, and salt. By ebullition and evaporation these solutions became concentrated until, saturation resulting, precipitation commenced, forming the necklike masses of salt, gypsum, and dolomite now encountered. With the cooling of the intrusive masses and the choking of the vents the process practically ceased. A period of subsidence followed, during which the coastal Quaternary beds, which at present cap the mounds, were laid down, followed by a secondary movement along the old lines of weakness, resulting in the present elevation of the mounds above the surrounding prairie.

Fenneman [6] discusses the domes and says:

> Both the abnormal temperatures and the abnormal salinity suggest upward movements of ground waters. Further study may perhaps show that ground waters have been concerned in making the salt and gypsum of the mounds, as well as the crystalline limestone. * * * It may even appear that the pressure exerted during the growth or alteration of these bodies was sufficient to raise the mounds.

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[1] Hahn, F. F., The form of salt deposits; Econ. Geology, vol. 7, pp. 120–125, 1912.

[2] Harris, G. D., Rock salt, its origin, geological occurrences, and economic importance in the State of Louisiana: Louisiana Geol. Survey Bull. 7, p. 59, 1908.

[3] Hill, R. T., The coast prairie of Texas: Science, vol. 14, p. 326, 1901.

[4] Hill, R. T., The Beaumont oil field, with notes on other oil fields of the Texas region: Franklin Inst. Jour., vol. 154, pp. 273–281, 1902.

[5] Hager, Lee, The mounds of the southern oil fields: Eng. and Min. Jour., vol. 78, pp. 137–139, 180–182, 1904. It appears that the idea of a volcanic neck or plug was in the minds of A. F. Lucas and others some time before this.

[6] Fenneman, N. M., Oil fields of the Texas-Louisiana Gulf Coastal Plain: U. S. Geol. Survey Bull. 282, p. 121, 1906.

Harris,[1] in the publication already cited, goes on to inquire: "How can rising columns of water be made to precipitate their salt, even though saturated, and, second, what is the force that lifts up a certain hundred or thousand feet of superficial strata in limited areas, almost never 2 miles across?" In brief, he answers: "Precipitation is due to decrease in temperature; and, second, the requisite uplifting force is amply accounted for by the power of growing crystals."

Against the explanation in the last sentence, it may be noted that the solubility of gypsum, which frequently accompanies salt in many of the domes, increases with falling temperature. Moreover, two conditions must be assumed in this explanation of the domes, namely, that certain waters have been concentrated to the point of saturation and that the growth of new crystals takes place between rigid solids and not in free brine. Although it is true that the solubility of salt decreases with falling temperature, the change is small. The amount of salt that will precipitate from a cubic meter of saturated brine on cooling from 60° to 20° C. is about 11 kilograms. This salt will occupy a volume of about 5 liters. The brine, however, on cooling from 60° to 20° C. contracts to the extent of about 18 liters, so that if the brine were held stationary, instead of moving and being continuously replenished, there would be a decided net contraction instead of an expansion. Evidently no expansive force could be exerted by the cooling brine. The force sufficient to open up or to maintain channels for continued circulation would have to be exerted entirely by the solid crystals of salt. The deposition of the 11 kilograms of salt, cited in the illustration, would leave 883 kilograms of water saturated with 317 kilograms of salt as a brine taking no part in the process, so that the amount of brine necessary to form a dome by deposition due to cooling would be very large. Although the disposition of this relatively large amount of brine can be explained by saying that it merely escaped at the surface, the theory of evaporation by natural gas could not only account for an initial concentration of the waters but also for the deposition of almost 30 times as much salt as could be deposited by the simple cooling of a saturated brine. In other words, the quantities of salt water required for the formation of the domes by deposition due to evaporation are much less than those required by the theory of deposition due to cooling.

On the hypothesis of a cooling brine, then, we calculate that a cubic meter of saturated brine would deposit 11 kilograms of salt on cooling from 60° to 20° C., whereas the same amount of salt could be deposited from such brine, through evaporation, by the escape of 790 cubic meters of gas at 40° C., 307 cubic meters at 60° C., or 74 cubic meters at 100° C. If the gas expands a hundredfold at the temperatures mentioned, the volumes of compressed gas required would be only about a hundredth of those mentioned. In short, the volumes of compressed gas would have to be from 24 to 260 times greater than a given volume of brine to leave salt as the final product under reasonably favorable conditions. The volumes of gas required are 145 and 1,550 times the volume of salt formed at 100° C., and 40° C., respectively. Looked at in another way, 1 cubic meter of brine could deposit 11 kilograms of salt by cooling or 330 kilograms by evaporation.

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[1] Harris, G. D., op. cit., p. 76.

A factor which, so far as we know, has not been mentioned as a cause for the deposition of the salt forming the domes is the change in the solubility of the salt with a change of pressure. The solubility of salt at 24.05° C. increases from 35.90 parts per 100 parts of water under a pressure of 1 atmosphere, to 37.36 parts under a pressure of 1,500 atmospheres.[1] Although this change is small, it may be effective where saturated solutions move upward from regions of very great pressure. It is comparable with the small change in solubility with change of temperature, which is the basis of Harris's theory, and the two factors influencing the solubility may act concomitantly.

Several European geologists have recently revived the old and long-neglected view that salt-dome structure is due to the flow of salt made plastic by pressure.[2] Lachmann[3] calls attention to the variety of deformations found in the German salt deposits and shows that the structural features range from those that are entirely conformable to the strata in which the salt deposits are found to those of domes which show practically no relation to the adjoining strata, having apparently been formed by the flowage of salt. Arrhenius[4] has discussed some of the physical and chemical problems involved in the formation of the German salt deposits and applies the principles of isostasy to explain the salt column in Drake's Saline, La. Before this explanation can be accepted, experiments upon the plastic flow of salt, with special reference to the effect of temperature and pressure, the action of water, and the possibility of flow by fracturing and granulation, followed by recementation and recrystallization are needed. Inasmuch as Arrhenius assumes that solutions have acted to some extent as a lubricant for the movement of the salt and also that many of the unusual structural forms found in the German potash salts are due to rearrangements brought about by water given off from hydrated minerals at depth, we feel that, even if the preceding views are accepted, the evaporation of solutions by gases is worthy of consideration.

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[1] Smithsonian physical tables, p. 143, 1916.

[2] Grupe, O., Zechsteinformation und ihr Salzlager im Untergrunde des hannoverschen Eichsfelds: Zeitschr. prakt. Geologie, vol. 17, p. 185, 1909. Harbort, E., Geologie der nordhannoverschen Salzhorste: Deutsch. geol. Gesell. Monatsber., 1910, p. 326, Lachmann, Richard, Salinare Spalteneruption gegen Eksemtheorie: Idem, p. 597, Stille, H., Aufsteigen des Salzgebirges: Zeitschr. prakt. Geologie, vol. 19, p. 91, 1911.

[3] Lachmann, Richard, Der Salzauftrieb, Halle, 1911. Separate from Kali, vol. 4. Nos. 8, 9, 22, 23, and 24, 1910. Studien ueber den Bau von Salzmassen: Idem, vol. 6, pp. 342–353, 366–375, 397–401, 418–431, 1913.

[4] Arrhenius, Svante, Zur Physik der Salzlagerstätten: Meddelanden k. v. Nobelinstitut, vol. 2, No. 20, 25 pp., 1912.

Conditions of comparative weakness that might permit the plastic flow of salt under great pressure would also permit the movement and probably the escape of solutions and gases, especially where the movements of salt were accompanied by faulting and fracturing of the overlying strata. Probably no one of the theories we have cited will suffice to explain all the unusual phenomena of salt domes, but it is evident that in conjunction with any of the processes mentioned the evaporation of water into moving and expanding gas must be regarded as important.

### AMOUNT OF GAS AVAILABLE FOR EVAPORATION.

Having shown that under reasonable conditions about 145 to 1,550 volumes of gas under a pressure of 100 atmospheres would be required to cause, through expansion and evaporation, the deposition of 1 volume of salt from a saturated solution, we must now consider whether the supply of gas is adequate to be considered a factor in the formation of salt domes in this way. It is difficult to decide the question positively, because little is known of the conditions involved, such as the thickness and character of the sediments in which gases might form and the dimensions and volumes of the salt masses. Even the origin of the gases is not known with certainty. Until the results of detailed studies, including deep boring, in the salt-dome region of Louisiana and Texas become available, calculations as to the quantity of gas available can have little value. Enormous volumes of gas are continuing to escape in the Gulf region, and we feel that although the amount of gas that has escaped is perhaps not sufficient to account for the complete development of the domes by this theory alone it is adequate to show that the theory sets forth at least one of the important factors in the development.

### ACCUMULATIONS OF GAS AND OIL ASSOCIATED WITH SALT DOMES.

In considering the escape of compressed natural gas we find that two facts are at once apparent. First, where deposits of natural gas occur only part of the available gas has escaped; second, under the conditions that permitted the escape of compressed gases part of the associated oil and water must also have escaped or migrated through the strata toward the regions of least pressure. These movements may have influenced the accumulation of gas and oil by facilitating the segregation of the hydrocarbons above the water and by causing the migration of gas and oil to favorable rock entrapments or reservoirs. It is not improbable that the accumulations of natural gas and petroleum associated with the salt domes have been formed partly in this way. Evidence that this principle is widely applicable to gas and oil deposits is furnished by the relatively complete segregation of gas and oil above water in the sharply folded, more or less fissured anticlines of certain fields and the relatively incomplete segregation that has taken place in the gentle folds of the Appalachian fields.

Among the factors that have retarded the escape of gas, oil, and water the sealing of the rock ~~passages by the deposition of mineral matter has been~~ of prime ~~importance~~. A common surface indication of petroleum and natural gas in some localities is the occurrence of fissures sealed by calcite or even by certain solidified hydrocarbons themselves.

Where salt masses similar to those in Louisiana and Texas are unaccompanied by gas and oil, it may be assumed, if the salt masses are held to have originated in part through the evaporative action of natural gases, that the escape of the gases has been relatively complete. As bituminous matter and carbonaceous shales are associated with many of the European salt masses, where but little gas or oil is now present, this view seems perfectly reasonable.

## INDUCED SEGREGATION OF OIL AND GAS.

During the more or less extensive movements through water-saturated sands, which occur incidentally to the extraction of oil and gas and which facilitate evaporation and concentration, oil and gas tend to segregate above the water in the higher portions of the pay sands. This process we have termed induced segregation.[1] The movements by which the segregation is facilitated are caused by the expansion of gas under pressure, either assisted or retarded by hydrostatic pressure, the tendency being to replace the materials extracted through the wells.

It has not been possible to measure the extent of the movements in the sands, but by studying the porosity and thickness of the sands and by calculating the volumes of rock necessary to contain the vast quantities of oil and water that have been produced in some of the fields, it is possible to approximate roughly the extent of migration. In Monroe County, Ohio, there is evidence that production from oil wells is accompanied by movements of water, oil, and gas through the Keener sand for distances ranging from half a mile to 1½ miles. Such migrations, we believe, must involve considerable segregation of gas and oil above the water.

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[1] Mills, R. V. A., and Wells, R. C., The evaporation of water at depth by natural gases (abstract) : Washington Acad. Sci. Jour., vol. 7, pp. 309–310, 1917.

The principles of induced segregation are worthy of consideration in the practical recovery of oil and gas. It is partly due to this segregation that certain wells which penetrate the higher parts of a water-saturated pay sand yield oil and gas more persistently than wells which penetrate lower parts of the same sand. In sands which are only partly filled with water or in which the water level is lowered during production induced migration and segregation will still occur, but the oil will not necessarily be found in the higher portions of the pay sands. A particular part of a pay sand may become so enriched by induced migration and segregation as to increase the rate of oil production from a certain well or group of wells, whereas the rate of production from neighboring wells will continually decrease until the wells are abandoned. The abandonment of wells yielding large amounts of water with relatively little oil may have a detrimental effect upon neighboring wells by decreasing the movements that bring about induced segregation, or by permitting the so-called "drowning out" of the productive wells by water. Many wells that have been abandoned because of their excessive yields of water might have been successfully operated had the geologic conditions and rearrangements of fluids been understood. Where the supply of deep-seated water is very large, the continued pumping of poorly productive wells that tap relatively high portions of pay sands should bring about increased oil production through induced migration and segregation unless the textural conditions in the sand are unfavorable. On the other hand, where the water level is lowered by pumping, wells penetrating relatively low portions of the pay sand may be benefited. Numerous examples justifying these statements have been noted during the field investigations for this paper.

Near Miltonsburg, Monroe County, Ohio, a Keener well had an initial daily yield of 1½ barrels of oil, with 150 barrels of water. By persistently pumping the well for one month the rate of oil production was slightly increased. At the end of 16 months the daily production was 5 barrels of oil, with 80 barrels of water. During the same period the rate of oil production from a neighboring well increased from 4 to 7 barrels of oil a day, while the rate of water production decreased from 100 to 25 barrels a day. Within distances of 500 to 2,000 feet wells drilled a few months previously and apparently yielding oil and water from the same pay sand were gradually producing less oil and more water. It appears that the increased production from two of the wells was due to deep-seated movements and rearrangements of the fluids, induced segregation being facilitated by conditions of structure, lenticularity, or texture of the productive sand.

In sec. 13, Center Township, Monroe County, Ohio, two Keener oil wells have yielded more than 80,000 barrels of oil and 250,000 to 300,000 barrels of salt water, the total volume of which (oil and water combined) appears to be enough to fill the productive sand completely throughout an area of at least 1 square mile. Nevertheless these two wells are surrounded by 11 so-called dry holes and two poorly productive oil wells at distances of only a few hundred to a few thousand feet. The two best wells tap a relatively high part of the pay sand, the top of which is 6 to 9 feet higher than in the surrounding wells, and have been operated steadily since 1906. In the poorly productive and nonproductive wells larger quantities of salt water with relatively little oil were encountered in lower portions of the same pay sand. The water together with oil seems, unquestionably, to have migrated to the productive wells during their operation.

A somewhat similar instance of induced migration and segregation was noted near Jerusalem Village, in Sunsbury Township, Monroe County, Ohio, where a small group of Keener oil wells has yielded approximately 120,000 barrels of oil together with 400,000 or 500,000 barrels of salt water. Of these amounts a single well on the J. R. Scott farm has yielded approximately 80,000 barrels of oil and 150,000 barrels of salt water. The top of the pay sand in this very productive well is 15 feet higher than in the surrounding wells. Furthermore this well was drilled in 1904 and has yielded oil and water steadily, whereas most of the other wells within distances of a few hundred to a few thousand feet have been abandoned because of the excessive yields of water with comparatively little oil.

Detailed field investigations by Munn[1] suggest that induced migration and segregation may be important factors in the recovery of oil from the Hundred-foot and other water-bearing sands in the Sewickley quadrangle. The significance of hydraulic movements in oil and gas accumulation was emphasized by Munn[2] in 1909, and what we have said regarding induced migration, segregation, and accumulation of gas and oil can be regarded as an outgrowth from his work.

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[1] Munn, M. J., Geology of the oil and gas fields in Sewickley quadrangle: Pennsylvania Top. and Geol. Survey Comm. Rept. 1, 1910.

[2] Munn, M. J., The anticlinal and hydraulic theories of oil and gas accumulation: Econ. Geology, vol. 4, pp. 509–529, 1909.

## CLOGGING OF OIL AND GAS SANDS.

Another process that has an influence on the extraction of oil and gas and is closely related to this investigation is the deposition of mineral matter in the interstices of a pay sand after extraction has begun. The clogging of the interstices may seal a pay sand sufficiently to retard or stop production from a well or group of wells long before the gas and oil are exhausted. Part of the trouble attributed to the paraffining of oil wells is no doubt due to the clogging of the sands by the deposition of mineral salts. As the result of chemical changes, such as those which are expressed by the type reaction set forth on page 50 and which are brought about through the mixing and concentration of certain waters having different properties of reaction, carbonates and sulphates are commonly deposited, not only in the wells and in the interstices of the productive sands immediately around the wells but also in portions of the sands that are remote from the wells. In this way many oil fields where the sands have been flooded by injurious waters have been ruined. A new well drilled in an old field where much oil and gas remain unextracted may be nonproductive owing to such clogging of the sands.

Waters that on being concentrated deposit carbonates or that react with the deep-seated brines to form carbonate or sulphate should be carefully excluded from all productive sands. If such waters have entered the productive sands or if it is impossible to exclude them from wells it may be feasible to use chemical reagents to prevent the deposition of mineral matter in the wells and the sand interstices or to remove such material which has previously been deposited. A detailed discussion of the practical methods of preventing or removing these mineral deposits would be inappropriate in this bulletin, though the subject is worthy of further investigation.

## PROSPECTING FOR OIL AND GAS.

In prospecting for oil and gas in a region known to be petroliferous the mere presence or absence of water in a deep-seated sand is frequently an important consideration. Thus, in prospecting the Hundred-foot sand for oil in western Pennsylvania, the operators welcome the presence of water in the sand, because as a rule in that region wells yielding mixtures of oil and water last longer and are more profitable.

From the analyses of Appalachian oil and gas field waters that are available, it appears that sulphates are characteristically lacking in the waters associated with the oil and gas, but that they are present in considerable proportions in the waters from shallow, nonpetroliferous rocks overlying oil and gas bearing deposits. Sulphates also occur in noteworthy amounts in waters from the deep-seated nonpetroliferous rocks in many places outside of oil and gas fields. Rogers[1] has described the application of these facts to the search for oil and gas in California, where for a number of years the absence of sulphates from deep-seated waters has been considered one indication of the proximity of oil or gas. The same principle may be applicable in the Appalachian as well as other fields, although the presence of barium and strontium in certain deep-seated brines may afford an explanation for the absence of sulphates in these waters.

The concentrated chloride waters associated with oil and gas in the Appalachian fields, besides lacking sulphates, also generally lack carbonate but contain noteworthy proportions of calcium. The calcium, together with sodium and magnesium, is deposited as chloride on complete evaporation. How generally this distinction holds true in waters outside of the Appalachian fields can be determined only by further study, but in prospecting for oil and gas in any field it should be advantageous to determine the characteristics of the waters associated with oil and gas in the nearest productive territory as compared with the waters in nonproductive strata.

In proved territory the presence or absence of newly deposited carbonates in the interstices of a pay sand suggests whether or not that part of the sand has been influenced by former production. If, for instance, oil, gas, and water have been drawn from that part of the sand, carbonates have probably been deposited in consequence of the liberation of carbon dioxide, together with other gases, from the water. Also if the sand has been flooded by waters leaking in from abandoned or poorly plugged wells the fact may be recognized through the presence of newly deposited carbonates in the interstices of the pay sand, through the low concentration of the constituents in the water, or through the high proportion of sulphate and carbonate in those constituents.

## DETERMINING THE SOURCE OF INFILTRATING WATERS.

Some of the detrimental effects produced when waters of certain types leak into wells and flood oil and gas sands have been sufficiently described to emphasize the importance of excluding injurious waters from the wells. To do this most effectively the source of an infiltrating water that is causing damage to a well, a group of wells, or the productive sands themselves should be determined and appropriate efforts made to stop the leaks. Studies of the waters occurring in the different strata in any particular field and of the probable reactions and precipitation that might ensue when such waters are mixed, concentrated, or diluted to form new solutions should throw valuable light upon this subject, if supplemented by studies of freshly formed mineral deposits and solutions collected from wells actually affected by infiltrating waters.

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[1] Rogers, G. S., Chemical relations of the oil-field waters in San Joaquin Valley, Cal.: U. S. Geol. Survey Bull. 653, 1917.

It is evident, for instance, that the injurious sulphate deposits which have interfered with the production of oil from certain old wells in Butler County, Pa., are due to the infiltration of sulphate-bearing waters from the shallow nonpetroliferous beds, the sulphate having reacted with soluble barium and strontium salts of the deep-seated brines in the wells where the leaks occurred. Carbonates are similarly deposited in some of these old wells in consequence of the infiltration from shallow beds of primary alkaline waters which react with the deep-seated brines as explained on page 50. The shallow waters causing these deposits have not been properly excluded from the wells in which the deposits are formed.

## NEED FOR FURTHER INVESTIGATION.

In concluding this paper we would emphasize the need for further investigation of the relations between the occurrence and production of petroleum and natural gas and the chemistry of the associated waters. Preliminary studies give proof of the value of such work, and there can be no doubt that future analytical and experimental studies will furnish additional criteria to be applied.

Where oil and gas are being drawn from water-bearing strata, careful consideration should be given to the mode of occurrence of the gas, oil, and water; the movements and rearrangements they undergo incident to extraction, especially with relation to structure, texture, and lenticularity of the sands; the physical and chemical changes that the waters undergo; the effects of these changes on the reservoir rocks and well casings and tubings; the effects that infiltrating waters of certain types have on the reservoir rocks and wells owing to concentration and to chemical reaction and precipitation; ~~and the methods of~~ remedying these effects and their causes.

The prevention of the formation of inorganic deposits in oil and gas sands and in wells, together with the removal of such deposits through the use of chemical reagents, constitutes in itself an important field for study. The application of knowledge of the chemistry of oil-field waters in the exclusion of infiltrating waters from wells or in the sealing and plugging of wells is also important. If well tubings and productive sands become clogged by inorganic deposits from oil-field waters, it may be feasible to utilize knowledge of the processes involved to exclude injurious waters from wells. The waters themselves may be made to furnish cementing material. Further consideration of these and other technologic phases of the study of oil and gas field waters is outside the province of this paper but presents an inviting field for investigation.

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